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THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY
III

THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

FOURTH EDITION (Revised and Enlarged)

VOL. III

WITH ILLUSTRATIONS

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FOREWORD

Volume III has been constructed on the same lines as those followed in Volume II. The Foreword written in Volume II therefore covers all that it is necessary to say concerning Volume III.

Dr. Johnson says in the Preface to his Dictionary, published in 1755, "*It is the fate of those who toil at the lower employments of life to be rather driven by the fear of evil, than attracted by the prospect of good; to be exposed to censure, without hope of praise; to be disgraced by miscarriage, or punished for neglect, where success would have been without applause, and diligence without reward.*

"*Among these unhappy mortals is the writer of dictionaries; whom mankind have considered, not as the pupil, but the slave of science, the pionier of literature, doomed only to remove rubbish and clear obstructions from the path of Learning and Genius, who press forward to conquest and glory, without bestowing a smile on the humble drudge that facilitates their progress. Every other author may aspire to praise; the lexicographer can only hope to escape reproach, and even this negative recompense has been yet granted to very few.*

"*. . . This recommendation of steadiness and uniformity does not proceed from an opinion, that particular combinations of letters have much influence on human happiness; or that truth may not be successfully taught by modes of spelling fanciful and erroneous: I am not yet so lost in lexicography, as to forget that 'words are the daughters of earth, and that things are sons of heaven.' Language is only the instrument of science, and words are but the signs of ideas: I wish, however, that the instrument might be less apt to decay, and that signs might be permanent, like the things which they denote.*

"*. . . To deliberate whenever I doubted, to enquire whenever I was ignorant, would have protracted the undertaking without end, and, perhaps, without much improvement; for I did not find by my first experiments, that what I had not of my own was easily to be obtained: I saw that one enquiry only gave occasion to another, that book referred to book, that to search was not always to find, and to find was not always to be informed; and that thus to persue perfection, was, like the first inhabitants of Arcadia, to chace the sun, which, when they had reached the hill where he seemed to rest, was still beheld at the same distance from them.*

"*. . . I look with pleasure on my book, however defective, and deliver it to the world with the spirit of a man that has endeavoured well. That it will immediately become popular I have not promised to myself: a few wild blunders, and risible absurdities, from which no work of such multiplicity was ever free, may for a time furnish folly with laughter, and harden ignorance in contempt; but useful diligence will at last prevail, and there never can be wanting some who distinguish desert; who will consider that no dictionary of a living tongue ever can be perfect . . . even a whole life would not be sufficient; that he, whose design includes whatever language can express, must often speak of what he does not understand; that a writer will sometimes be hurried by eagerness to the end, and sometimes faint with weariness under a task, which Scaliger compares to the labours of the anvil and the mine; that what is obvious is not always known, and what is known is not always present; that sudden fits of inadvertency will surprize vigilance, slight avocations will seduce attention, and casual eclipses of the mind will darken learning; and that the writer shall often in vain trace his memory at the moment of need, for that which yesterday he knew with intuitive readiness, and which will come uncalled into his thoughts to-morrow.*"

There can be no doubt that the great man had his tongue in his cheek when he wrote this wonderful Preface. Few men have suffered less from an inferiority complex than Dr. Johnson, prince of lexicographers, and there is no question but that he was merely hanging out a bait for those who were willing to offer praise rather than censure and pay him the tribute he so dearly loved to receive. On the whole, however, we are in the fortunate position of having had a wide number of reviews from all parts of the world which have been both laudatory and fair. The number of adverse criticisms have been amazingly small and to those who have written them we recommend the quotation given above.

We have again to thank Dr. J. N. Goldsmith for his valuable assistance in reading the proof.

We wish also to thank all those who have contributed to the Volume and those whose names are mentioned in the Prefaces to Vols. I and II for the work they have been so kind as to do for us.

The spelling of botanical names is still a controversial subject and we acknowledge gratefully much kind help we have received from the Librarian and Deputy Librarian of the Royal Botanic Gardens, Kew.

JOCELYN THORPE
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South Kensington,
March, 1939.

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ABBREVIATIONS

OF THE TITLES OF JOURNALS, ETC.

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A. I; *A.* II; *A.* III	British Chemical and Physiological Abstracts.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Acta Bot. Fennica	Acta Botanica Fennica.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicæ	Acta Societatis Scientiarum Fennicæ.
Agric. Eng.	Agricultural Engineering.
Agric. Gaz. New South Wales	Agricultural Gazette of New South Wales.
Agric. J. Brit. Guiana	Agricultural Journal of British Guiana.
Agric. Live-stock India	Agriculture and Live-stock in India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Reports and Bulletins.
Allgem. Oel- Fett-Ztg.	Allgemeine Oel- und Fett-Zeitung.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Aluminium	Aluminium.
Amer. Chem. Abstr.	Chemical Abstracts. Published by the American Chemical Society.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. Gas J.	American Gas Journal.
Amer. Ink Maker	American Ink Maker.
Amer. Inst. Min. Met. Eng. Publ.	American Institute of Mining and Metallurgical Engineers Publication.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health and the Nation's Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Paint J.	American Paint Journal.
Amer. Potato J.	American Potato Journal.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Anal. Inst. invest. cient. tecn.	Anales del Instituto de investigaciones científicas y tecnológicas.
Analyst	Analyst.
Anat. Rec.	Anatomical Record.
Angew. Bot.	Angewandte Botanik.
Angew. Chem.	Angewandte Chemie (changed from Z. angew. Chem. in 1932).
Anilinokras. Prom.	Anilinokrasotschnaja Promischlennosti.
Ann. Acad. Brasil. Sci.	Annals da Academia Brasileira de Sciencias.
Ann. Acad. Sci. Fennicæ	Annales Academiæ Scientiarum Fennicæ.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomique.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Ann. di Bot.	Annali di Botanica.
Ann. Falsif.	Annales des Falsifications.
Ann. Ferm.	Annales des Fermentations.
Ann. Inst. Anal. Phys. Chim.	Annales de l'Institut d'Analyse Physico-chimique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Mines Belg.	Annales des Mines de Belgique.

Ann. Off. nat. Comb. liq.	Annales de l'Office nationale des Combustibles liquides.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. Sect. Platine	Annales du Secteur Platine et des autres Métaux Précieux.
Ann. Sci.	Annals of Science.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Sci. Bruxelles	Annales de la Société Scientifique de Bruxelles.
Apoth.-Ztg.	Apotheker-Zeitung.
Arb. Biol. Reichanst. Land- u. Forstwirts.	Arbeiten der Biologisches Reichanstalt fur Land- und Forstwirtschaft.
Arbeitsphysiol.	Arbeitsphysiologie.
Arch. Biol.	Archives de Biologie.
Arch. Eisenhüttenw.	Archiv. für das Eisenhüttenwesen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Gewerbepath. Gewerbehyg.	Archiv für Gewerbepathologie und Gewerbehygiene.
Arch. Hyg. Bakt.	Archiv der Hygiene und Bakteriologie.
Arch. Int. Med.	Archives of Internal Medicine.
Arch. int. Physiol.	Archives internationales de Physiologie.
Arch. Ist. Biochim. Ital.	Archivio dello Istituto Biochimico Italiano.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Min. Soc. Sci. Varsovie	Archives de Minéralogie de la Société des Sciences de Varsovie (Archivum Mineralogiczne Towarzystwa Naukowego Warszawskiego).
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. Physiol.	Archives Néerlandaises de Physiologie de l'Homme et des Animaux.
Arch. Pflanzenbau	Archiv. für Pflanzenbau.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Protistenk.	Archiv für Protistenkunde.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arch. Tierernährung u. Tierzucht	Archiv für Tierernährung und Tierzucht.
Arch. Wärmewirts.	Archiv für Wärmewirtschaft.
Arizona Agric. Exp. Sta. Bull.	Arizona Agricultural Experiment Station Bulletin.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysics Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts. B.—Applied Chemistry.
B.P.	British Patent.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Ges. Kohlentech.	Berichte der Gesellschaft für Kohlentechnik.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. Ukrain. Wiss. Forsch. physikal. Chem.	Berichte des Ukrainischen Wissenschaftlichen Forschungsinstituts für physikalische Chemie.
Berlin. klin. Woch.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Bied. Zentr. (Tierernähr.)	Biedermann's Zentralblatt (Tierernährung).
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biochimia	Biochimia.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacíonal des Ciencias, Cordoba.
Bol. Soc. Quim. Peru	Boletin de la Sociedad Quimica del Peru.
Boll. Chim. farm.	Bollettino Chimico-Farmaceutico.
Boll. Sez. Ital.	Bolletino della Sezione Italiana.
Boll. Soc. Geol. Ital.	Bollettino della Società Geologica Italiana.
Boll. Soc. Ital. Biol. sperim.	Bolletino della Società Italiana di Biologia sperimentalla.
Boll. Soc. Med-.Chirurg.	Bollettino della Società Medico-Chirurgica, Pavia.
Boll. Uff. Staz. Sperim. Ind. Essenze.	Bollettino Ufficiale della R. Stazione Sperimentale per l'Industria delle Essenze e dei Derivati dagli Agrumi in Reggio Calabria.

Boll. Uff. Staz. Sperim. Ind. Pelli.	R. Stazione Sperimentale per l'Industria delle Pelli e delle materie concianti, Bollettino Ufficiale.
Bot. Archiv	Botanisches Archiv.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Braunkohlenarchiv	Braunkohlenarchiv.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. Dental J.	British Dental Journal.
Brit. Guiana Dept. Agric. Bull.	British Guiana Department of Agriculture Bulletin.
Brit. J. Exp. Path.	British Journal of Experimental Pathology.
Brit. J. Phot.	British Journal of Photography.
Brit. J. Phys. Med.	British Journal of Physical Medicine.
Brit. Med. J.	British Medical Journal.
Brit. Plastics	British Plastics and Moulded Products Trader.
Bul. Chim.	Buletinul Chimie.
Bul. Chim. Soc. Române	Buletinul de Chimie pura si aplicata al Societatii Române de Chimie.
Bul. Soc. Chim. România	Buletinul Societătii de Chimie din România.
Bul. Soc. Fiz. România	Buletinul Bilunar al Societătii de Fizică din România.
Bul. Soc. Române Stiin.	Buletinul Societatii Române de Stiinte.
Bull. Acad. Méd. Roumanie	Bulletin de l'Académie de Médecine de Roumanie.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Agra & Oudh	Bulletin of the Academy of Sciences of Agra and Oudh.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Agric. Chem. Soc. Japan	Bulletin of the Agricultural Chemical Society of Japan.
Bull. Amer. Ceram. Soc	Bulletin of the American Ceramic Society.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Biol. Méd. exp. U.R.S.S.	Bulletin de Biologie et Médecine expérimentale de l'U.R.S.S.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Dept. Agric. Kenya	Bulletin of the Department of Agriculture of Kenya.
Bull. Dept. Agric. South Africa	Bulletin of the Department of Agriculture of South Africa.
Bull. Entomol. Res.	Bulletin of Entomological Research.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikagaku Kenkyujo Ihō).
Bull. Inst. Pin	Bulletin de l'Institut du Pin.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Mat. Grasses	Bulletin des Matières Grasses.
Bull. Photogrammétrie	Bulletin de Photogrammétrie.
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association.
Bull. School Mines and Met., Univ. Missouri.	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Sericult. Japan	Bulletin of Sericulture and Silk Industry, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Chim. Yougoslav.	Bulletin de la Société Chimique du Royaume de Yougoslavie.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. Franç. Min.	Bulletin de la Société Française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie et de Cinématographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Sci. Hyg. aliment.	Bulletin de la Société Scientifique d'Hygiène alimentaire.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.

Canad. Chem.	Canadian Chemistry and Process Industries.
Canad. Chem. Met.	Canadian Chemistry and Metallurgy.
Canad. Dairy & Ice Cream J.	Canadian Dairy and Ice Cream Journal.
Canad. J. Res.	Canadian Journal of Research.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cellulosechem.	Cellulosechemie.
Cement and Lime Manuf.	Cement and Lime Manufacture.
Cereal Chem.	Cereal Chemistry.
Chaleur et Ind.	Chaleur et Industrie.
Chem. Age	Chemical Age.
Chem. App.	Chemische Apparatur.
Chem. Eng. Min. Rev.	Chemical Engineering and Mining Review.
Chem. Erde	Chemie der Erde.
Chem. Fabr.	Die Chemische Fabrik.
Chem. and Ind.	Chemistry and Industry.
Chem. Ind.	Chemische Industrie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vedu a Průmysl."
Chem. Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Soc. Annual Rep.	Annual Reports on the Progress of Chemistry.
Chem. Obzor.	Chemický Obzor.
Chem. Social. Agric.	Chemisation of Socialistic Agriculture (U.S.S.R.).
Chem. Trade J.	Chemical Trade Journal.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Cheshunt Agric. Exp. Sta. Ann. Rep.	Cheshunt Agricultural Experiment Station Annual Reports.
Chim. e l'Ind.	La Chimica e l'Industria.
Chim. et Ind.	Chimie et Industrie.
Chinese Med. J.	Chinese Medical Journal.
Chinese J. Physics.	Chinese Journal of Physics.
Chinese J. Physiol.	Chinese Journal of Physiology.
Coal Age	Coal Age.
Coal Carbonisation	Coal Carbonisation.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemica Communications.
Coll. Eng.	Colliery Engineering.
Coll. Guard.	Colliery Guardian.
Collegium	Collegium.
Colorado Agric. Exp. Sta. Bull.	Colorado Agricultural Experiment Station Bulletin.
Combustion	Combustion.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Contr. Boyce Thompson Inst.	Contributions from Boyce Thompson Institute.
Cornell Univ. Agric. Exp. Sta. Bull.	Cornell University Agricultural Experiment Station Bulletin.
Current Sci.	Current Science.
Cyprus Agric. J.	Cyprus Agricultural Journal.
Dairy Ind.	Dairy Industry.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Delaware Agric. Exp. Sta. Bull.	Delaware Agricultural Experiment Station Bulletin.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Zuckerind.	Die Deutsche Zuckerindustrie.
East Malling Res. Sta., Ann. Repts., etc.	East Malling Research Station, Annual Reports, etc.
Ecology	Ecology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Empire Cotton Growing Rep. Exp. Sta.	Empire Cotton Growing Reports of the Experimental Station.

Empire Cotton Growing Rev.	Empire Cotton Growing Review.
Empire J. Exp. Agric.	Empire Journal of Experimental Agriculture.
Engineer	Engineer.
Engineering	Engineering.
Eng. and Min. J.	Engineering and Mining Journal.
Enzymologia	Enzymologia.
Ergebn. Physiol.	Ergebnisse der Physiologie.
Ernährung	Die Ernährung.
Ernähr. Pflanze	Ernährung der Pflanze.
F.P.	French Patent.
Facts about Sugar	Facts about Sugar.
Farbe u. Lack	Farbe und Lack.
Farben-Chem.	Farben-Chemiker.
Farben-Ztg.	Farben-Zeitung.
Farve og Lak	Farve og Lak.
Fermentforsch.	Fermentforschung.
Fert. Feeding Stuffs J.	Fertiliser, Feeding Stuffs and Farm Supplies Journal.
Fette u. Seifen	Fette und Seifen.
Feuerfest	Feuerfest.
Feuerungstech.	Feuerungstechnik.
Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Flora	Flora.
Florida Agric. Exp. Sta. Bull.	Florida Agricultural Experiment Station Bulletin.
Food	Food.
Food Manuf.	Food Manufacture.
Food Res.	Food Research.
Forstarchiv	Forstarchiv.
Foundry Trade J.	Foundry Trade Journal.
Fruit Prod. J.	Fruit Products Journal.
Fuel	Fuel in Science and Practice.
Fuel Econ.	Fuel Economist.
Fuel Econ. Rev.	Fuel Economy Review.
G.P.	German Patent.
Gas Ind.	Gas Industry.
Gas J.	Gas Journal.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gas World	Gas World.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Georgia Agric. Exp. Sta. Bull.	Georgia Agricultural Experiment Station Bulletin.
Ges. Abh. Kennt. Kohle	Gesammelte Abhandlungen der Kenntnis der Kohle.
Glass Ind.	Glass Industry.
Glasshütte	Die Glasshütte.
Glückauf	Glückauf.
Gummi-Ztg.	Gummi-Zeitung.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hilgardia	Hilgardia.
Imp. Bur. Soil Sci. Tech. Comm.	Imperial Bureau of Soil Science, Technical Communications.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
Indian J. Vet. Sci.	Indian Journal of Veterinary Science.
Indian Lac Res. Inst. Bull.	Indian Lac Research Institute Bulletin.
India-rubber J.	India-rubber Journal.
Ind. Chem.	Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. [*Anal.*]	Industrial and Engineering Chemistry, Analytical Edition.
Int. Rev. Agric.	International Review of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Age	Iron Age.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scolarship Memoirs.
J.C.S.	Journal of the Chemical Society.

Jahrb. geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Japan. J. Med. Sci.	Japanese Journal of Medical Sciences.
Japan. J. Physics	Japanese Journal of Physics.
Japan Nickel Rev.	Japan Nickel Review.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Soc. Mech. Eng.	Journal of the American Society of Mechanical Engineers.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia.
J. Appl. Physics	Journal of Applied Physics (formerly Physics).
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Austral. Inst. Agric. Sci.	Journal of the Australian Institute of Agricultural Science.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Brit. Dairy Farmers' Assoc.	Journal of the British Dairy Farmers' Association.
J. Brit. Wood Pres. Assoc.	Journal of the British Wood Preserving Association.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Cancer Res. Comm. Sydney.	Journal of the Cancer Research Committee of the University of Sydney.
J. Cell. Comp. Physiol.	Journal of Cellular and Comparative Physiology.
J. Cellulose Inst. Tokyo	Cellulose Industry, Journal of the Cellulose Institute, Tokyo.
J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Eng. China	Journal of Chemical Engineering, China.
J. Chem. Ind. Russ.	Journal of Chemical Industry, Russia.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Physics	Journal of Chemical Physics.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys.	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Counc. Sci. Ind. Res. Australia.	Journal of the Council of Scientific and Industrial Research of Australia.
J. Dairy Res.	Journal of Dairy Research.
J. Dairy Sci.	Journal of Dairy Science.
J. Dept. Agric. I.F.S.	Journal of the Department of Agriculture of the Irish Free State.
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture, South Australia.
J. Dept. Agric. Victoria.	Journal of the Department of Agriculture, Victoria.
J. Dept. Agric. W. Australia	Journal of the Department of Agriculture, Western Australia.
J. Ecology	Journal of Ecology.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Egypt. Med. Assoc.	Journal of the Egyptian Medical Association.
J. Electrodep. Tech. Soc.	Journal of the Electrodepositors Technical Society.
J. Exp. Biol.	Journal of Experimental Biology.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.

J. Fuel Soc. Japan	Journal of the Fuel Society of Japan.
J. Gen. Chem. Russ.	Journal of General Chemistry, Russia (formerly J. Russ. Phys. Chem. Soc.).
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Indian Chem. Soc.	Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Ind. Hyg.	Journal of Industrial Hygiene and Toxicology.
J. Infect. Dis.	Journal of Infectious Diseases.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Inst. Electr. Eng.	Journal of the Institution of Electrical Engineers.
J. Inst. Fuel.	Journal of the Institute of Fuel.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Inst. Sewage Purif.	Journal of the Institute of Sewage Purification.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Min. Agric. N. Ireland	Journal of the Ministry of Agriculture of Northern Ireland.
J. New England Water Works Assoc.	Journal of the New England Water Works Association.
J. Nutrition	Journal of Nutrition.
J. Oil Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Org. Chem.	Journal of Organic Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
J. Physical Chem.	Journal of Physical Chemistry.
J. Phys. Chem. Russ.	Shurnal Fizitscheskoi Chimii.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium	Journal de Physique et le Radium.
J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Microscop. Soc.	Journal of the Royal Microscopical Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Roy. Tech. Coll.	Journal of the Royal Technical College (Glasgow).
J. Rubber Res.	Journal of Rubber Research.
J. Rubber Res. Inst. Malaya	Journal of the Rubber Research Institute of Malaya.
J. Sci. Hiroshima Univ.	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Sci. Tech. India	Journal of Science and Technology, India.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. South-East. Agric. Coll.	Journal of the South-Eastern Agricultural College, Wye, Kent.
J. State Med.	Journal of State Medicine.
J. Text. Inst.	Journal of the Textile Institute.
J. Univ. Bombay	Journal of the University of Bombay.

J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Kali	Kali.
Kautschuk	Kautschuk.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Agric. Exp. Stat. Bull.	Kentucky Agricultural Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloid. Shurn.	Kolloidni Shurnal.
Kolloid-Z.	Kolloid-Zeitschrift.
Kunststoffe	Kunststoffe.
Lait	Le Lait.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
London Shellac Res. Bur., Tech. Paper	London Shellac Research Bureau, Technical Paper.
Louisiana Planter	Louisiana Planter.
Malay. Agric. J.	Malayan Agricultural Journal.
Mass. Agric. Exp. Sta. Bull.	Massachusetts Agricultural Experiment Station Bulletin.
Materie Plast.	Materie Plastiche.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Med. Doświad.	Medycyna Doświadczalna i Społeczna.
Mem. Accad. Lincei	Memorie della Reale Accademia Nazionale dei Lincei.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Agric. Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Inst. Chem. Ukrain. Acad. Sci.	Memoirs of the Institute of Chemistry, Ukrainian Academy of Sciences.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Mém. Soc. Ing. Civ. France	Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civils de France.
Metal Ind.	Metal Industry.
Metal Progr.	Metal Progress.
Metall u. Erz	Metall und Erz.
Metallges. Rev.	Metallgesellschaft Periodic Review.
Metallurgia	Metallurgia.
Met. & Alloys	Metals and Alloys.
Metals Tech.	Metals Technology.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Mich. Agric. Exp. Sta. Bull.	Michigan Agricultural Experiment Station Bulletin.
Mikrochem.	Mikrochemie.
Milch. Forsch.	Milchwirtschaftliches Forschungen.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Milk Ind.	Milk Industry.
Milk Plant Month.	Milk Plant Monthly.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. & Met.	Mining and Metallurgy.
Missouri Agric. Exp. Sta. Res. Bull.	Missouri Agricultural Experiment Station Research Bulletin.
Mitt. Kohlenforschungsinst. Prag	Mitteilungen des Kohlenforschungsinstituts in Prag.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Mitt. Materialprüf.	Mitteilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mitteilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Mitt. Textilforsch. Krefeld	Mitteilungen der Textilforschungsanstalt Krefeld e.V.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.

Montana Agric. Exp. Sta. Bull.	Montana Agricultural Experiment Station Bulletin.
Month. J. Inst. Metals	Monthly Journal of the Institute of Metals.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Month. Rep. Dept. Agric. N. Ireland.	Monthly Reports of the Department of Agriculture of Northern Ireland.
Mühlenlab.	Das Mühlenlaboratorium.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Butter & Cheese J.	National Butter and Cheese Journal.
Nat. Paint Var. Assoc. Circ.	National Paint, Varnish, and Lacquer Association, Inc., Circular.
Nature	Nature.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
Naturwiss.	Die Naturwissenschaften.
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletin.
New Jersey Agric. Exp. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletin.
New Phytol.	New Phytologist.
New York Agr. Expt. Sta. Bull.	New York State Agricultural Experiment Station Bulletins.
New York (Geneva) Agric. Exp. Sta. Bull.	New York (Geneva) Agricultural Experiment Station Bulletin.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nutr. Abs.	Nutrition Abstracts and Reviews.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societétens Förhandlingar, Helsingfors.
Oel u. Kohle	Oel und Kohle.
Off. Digest	Official Digest of the Federation of Paint and Varnish Production Clubs.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletin.
Oil and Gas J.	Oil and Gas Journal.
Oil and Soap	Oil and Soap.
Oklahoma Agric. Exp. Sta. Bull.	Oklahoma Agricultural Experiment Station Bulletin.
Österr. Chem.-Ztg.	Österreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Pacific Pulp and Paper Ind.	Pacific Pulp and Paper Industry.
Paint Manuf.	Paint Manufacture.
Paint, Oil, and Chem. Rev.	Paint, Oil, and Chemical Review.
Paint Tech.	Paint Technology.
Paint and Var. Prod. Man.	Paint and Varnish Production Manager.
Paper	Paper.
Paper Ind.	Paper Industry.
Paper-Maker	Paper-Maker and British Paper Trade Journal.
Paper Trade J.	Paper Trade Journal.
Papier-Fabr.	Papier-Fabrikant.
Pedology	Pedology.
Peint., Pig., Ver.	Peinture, Pigment, Vernis.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Pflüger's Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Ztg.	Pharmazeutische Zeitung.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Philippine Agric.	Philippine Agriculturist.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physics	Physics (now Journal of Applied Physics).

Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sovietunion	Physikalische Zeitschrift der Sovietunion.
Phytopath.	Phytopathology.
Phytopath. Z.	Phytopathologische Zeitschrift.
Plant Physiol.	Plant Physiology.
Planta (Z. wiss. Biol.)	Planta (Zeitschrift für wissenschaftliche Biologie).
Plast. Massi	Plastitschekie Massi.
Poultry Sci.	Poultry Science.
Proc. Acad. Sci. Agra and Oudh	Proceedings of the Academy of Sciences of the United Provinces of Agra and Oudh, India.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Amer. Gas Assoc.	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy (Tokyo).
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Internat. Cong. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. Internat. Soc. Soil Sci.	Proceedings of the International Society of Soil Science.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leningrad Dept. Inst. Fert.	Proceedings of the Leningrad Departmental Institute of Fertilisers.
Proc. Muslim Assoc.	Proceedings of the Muslim Association for the Advancement of Science.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc., Vizianagram.	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. S. Wales Inst. Eng.	Proceedings of the South Wales Institute of Engineers.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section of the Paper Makers' Association of Great Britain and Ireland.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Protoplasma	Protoplasma.
Przemysł Chem.	Przemysł Chemiczny.
Publ. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Prírodovèdeckou Facoultou Masarykovy University).
Pulp and Paper Mag. Canada	Pulp and Paper Magazine of Canada.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Queensland J. Agric.	Queensland Journal of Agriculture.
Rayon Text. Month.	Rayon Textile Monthly.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.

Refiner	Refiner and Natural Gasoline Manufacturer.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rensselaer Polyt. Inst. Bull.	Rensselaer Polytechnic Institute Bulletin.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Res. Stud. State Coll. Washington	Research Studies of the State College of Washington.
Rev. Aluminium	Revue de l'Aluminium.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada, Ôrgão de Sociedade Portuguêsa de Química e Física.
Rev. Fac. Quím. Ind. Agric.	Revista de la Facultad de Química Industrial y Agrícola.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics.	Review of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sborn. Trud. Ukrain. Chim. Inst. Odessa	Sbornik Trudov Ukrainskogo Nautschno-Issledova-Telskogo Chimitscheskogo Instituta Odessa.
Science	Science.
Sci. Agric.	Scientific Agriculture.
Sci. and Cult.	Science and Culture.
Sci. et Ind.	Science et Industrie.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Mem. Univ. Saratov	Scientific Memoirs of the University of Saratov.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Quart. Nat. Univ. Peking	Science Quarterly of the National University of Peking.
Sci. Rep. Hiroshima Tech. Sch.	Scientific Reports of the Hiroshima Higher Technical School.
Sci. Rep. Tôhoku	Science Reports, Tôhoku Imperial University.
Sci. Rep. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Sect. Nat. Paint, Var. Assoc. Circ.	Scientific Section, National Paint, Varnish, and Lacquer Association, Inc., Circulars.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Scot. J. Agric.	Scottish Journal of Agriculture.
Seifens.-Ztg.	Seifensieder-Zeitung.
Sewage Works J.	Sewage Works Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collection.
Soap	Soap.
Soap Trade Rev.	Soap, Perfumery and Cosmetic Trade Review.
Soil Res.	Soil Research.
Soil Sci.	Soil Science.
Sparwirts.	Sparwirtschaft.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Stain Tech.	Stain Technology.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Steam Eng.	Steam Engineer.
Sugar Bull.	Sugar Bulletin.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Superphosphat	Superphosphat.
Superphosphate	Superphosphate.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tasmanian Agric. J.	Tasmanian Agricultural Journal.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp.
Tech. Publ. Tin Res. Counc.	Technical Publications of the International Tin Research and Development Council.
Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.

Teer u. Bitumen	Teer und Bitumen.
Tekn. Tidsk.	Teknisk Tidskrift.
Textilber.	Melliand Textilberichte.
Tids. Kjemi	Tidsskrift for Kjemi og Bergvesen.
Tonind.-Ztg.	Tonindustrie-Zeitung.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Amer. Soc. Mech. Eng.	Transactions of the American Society of Mechanical Engineers.
Trans. Amer. Soc. Met.	Transactions of the American Society of Metals.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Dokuchaiev Soil Inst.	Transactions of the Dokuchaiev Soil Institute.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Inst. Plast. Ind.	Transactions of the Institute of the Plastics Industry.
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry.
Trans. N. Eng. Inst. Min. Mech. Eng.	Transactions of the North of England Institute of Mining and Mechanical Engineers.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Opt. Soc.	Transactions of the Optical Society.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.
Trans. Saratov Univ.	Transactions of the Saratov University (Gelehrte Notizen der Saratover Staats Universität).
Trop. Agric.	Tropical Agriculturist (Ceylon).
Trop. Agric. (Trinidad)	Tropical Agriculture (Trinidad).
Tsch. Min. Mitt.	Mineralogische und Petrographische Mitteilungen (Zeitschrift für Kristallographie, Mineralogie, und Petrographie, Abteilung B).
U.S. Bur. Mines, Bull., Tech. Papers, and Rept. Invest.	United States Bureau of Mines, Bulletins, Technical Papers, and Reports of Investigations.
U.S. Bur. Plant Ind.	United States Bureau of Plant Industry.
U.S. Dept. Agric. Bull. (or Circ.)	United States Department of Agriculture Bulletins (or Circulars).
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
U.S. Publ. Health Rep.	United States Public Health Reports.
Ukrain. Biochem. J.	Ukrainian Biochemical Journal.
Ukrain. Chem. J.	Ukrainian Chemical Journal.
Union S. Africa Dept. Agric. Bulls.	Union of South Africa Department of Agriculture Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exp. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verfkroniek	Verfkroniek.
Verh. Geol. Reichsanst. Wien	Verhandlungen der Geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Vermont Agric. Exp. Sta. Bull.	Vermont Agricultural Experiment Station Bulletin.
Vet. Rec.	Veterinary Record.
Virginia (Blacksburg) Exp. Sta. Bull.	Virginia (Blacksburg) Experiment Station Bulletin.
Virginia Truck Exp. Sta. Bull.	Virginia Truck Experiment Station Bulletin.
Welsh J. Agric.	Welsh Journal of Agriculture.
Wiss. Veröff. Siemens-Werken	Wissenschaftliche Veröffentlichungen aus den Siemens-Werken.
Woch. Brau.	Wochenschrift für Brauerei.
World's Paper Tr. Rev.	World's Paper Trade Review.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.

Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Fleisch- Milch-Hyg.	Zeitschrift für Fleisch- und Milch-Hygiene.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Naturwiss.	Zeitschrift für die gesamte Naturwissenschaft.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Instrumkde.	Zeitschrift für Instrumentenkunde.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzanernährung, Düngung, und Bodenkunde (*title now changed to* Bodenkunde und Pflanzenernährung).
Z. Pflanzenkr. Pflanzenschutz.	Zeitschrift für Pflanzenkrankheiten (Pflanzenpathologie) und Pflanzenschutz.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. pr. Geol.	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Ing.	Zeitschrift Vereins deutscher Ingenieure.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (*now changed to* Z. Wirts. Zuckerind.).
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.
Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie (Vereins der deutschen Zucker-Industrie).
Z. wiss. Biol.	Zeitschrift für wissenschaftliche Biologie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuchtung	Zeitschrift für Zuchtung.
Z. Zuckerind. Czechoslov.	Zeitschrift für die Zuckerindustrie der Čechoslovakischen Republik.
Zavod. Lab.	Zavodskaja Laboratorija.
Zellstoff u. Papier	Zellstoff und Papier.
Zement	Zement.
Zentr. Bakt.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Min.	Zentralblatt für Mineralogie, Geologie und Paläontologie.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

A DICTIONARY OF APPLIED CHEMISTRY.

C—*continued.*

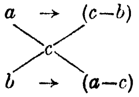
CHEMICAL CALCULATIONS. There are methods of saving time in calculating which although well known in some circles are not, it seems, so widely used as they deserve. The object of this article is to give a selection of methods, mainly of technical interest, used for various purposes.

Weighing by Swings.—A graph may be kept in the balance case on which is plotted the deflection caused by 1 mg. at different loads. On paper ruled in tenths of an inch with milligrams as ordinates and scale divisions as abscissæ, lines are ruled from 0 through the points indicating the deflections caused by 1 mg. at loads of 100, 50, 10, 1 g. Reference to the appropriate line will enable the final mg. of the weight to be read off without calculation.

Simplified Division of the type 124·712/99·926 may be carried out by adding 0·074 to the denominator and a proportionate number x to the numerator so that the fraction becomes $(124{\cdot}712+x)/100$. If $x=0{\cdot}07\times 12/10=0{\cdot}084$, the quotient is 1·24796; if $x=0{\cdot}074\times 125/100=0{\cdot}092$, the quotient is 1·24804. Calculated with five-figure logarithms the original division yields 1·2480, with seven-figure logarithms 1·24804. Since the fifth and fourth decimal places have usually no significance in technical work, the approximation is satisfactory.

Assay Ton.—This is an instance of a general method of avoiding calculations by the choice of a suitable weight of sample for analysis; for instance, in the analysis of ores of gold and silver where the amount of precious metal is expressed in oz. troy per ton of 2,000 lb. avoirdupois. If the weigh-out is 29·1666 g., the number of milligrams of silver or gold found is also the number of oz. troy per ton, since this ton contains 29166·6 oz. troy. Similarly, grains of x per gallon of a water may be estimated by titrating 70 ml. of the sample with a standard solution of which 1 ml.=1 mg. x, since 1 Imperial gallon of water weighs 70,000 grains. In each of the examples given 1 mg. is the same fraction of the amount taken for analysis as is the smaller of the two commercial units of the larger.

Mixtures.—A method of calculating the quantities of two solutions, A (of higher concentration, a) and B (of lower concentration, b) required to form a mixture of intermediate concentration c is shown by the diagram, which



indicates that the mixture consists of $(c-b)$ parts of A and $(a-c)$ parts of B. The symbols a and b may indicate normality or other measured property which is proportional to the concentration. Parts by volume may be used when there is no volume change on mixing. B may be water or a pure solvent of concentration 0.

H. Mager (Chem.-Ztg. 1910, **34**, 865) has published a collection of mixture-formulæ. The quantities of A and B required (symbols as in the preceding formula) for preparing a stated quantity M of a specified intermediate concentration c are given by the equations $x=\mathrm{M}(c-b)/(a-b)$, where x=parts of A, and $\mathrm{M}-x$ =parts of B. When a given number N of parts of B have to be made up to a mixture of concentration c, by adding x parts of A, $x=\mathrm{N}(c-b)/(a-c)$.

In the case that the two solutions A and B contain different solutes and that M parts of a mixture are required containing the solutes in the new proportions a'/b', $x=\mathrm{M}a'b/(a'b+b'a)$. The corresponding problem with three solutions A, B, and C, of concentrations a, b, and c respectively when the specified quantity M of mixture is to contain the solutes in the proportions $a' : b' : c'$ is solved by the equations

$$x_{\mathrm{A}}=\mathrm{M}a'bc/(a'bc+b'ac+c'ab).$$
$$x_{\mathrm{B}}=\mathrm{M}b'ac/(a'bc+b'ac+c'ab).$$
$$x_{\mathrm{C}}=\mathrm{M}-(x_{\mathrm{A}}+x_{\mathrm{D}}).$$

H. G. Nevitt (Chem. Met. Eng. 1932, **39**, 673) gives two charts and one table of formulæ for "weighted per cent. calculations," that is, the conversion of weight per cent. into mols. per cent., volumes per cent., etc.

The general formula is $\mathrm{P}'=\dfrac{100}{1+\mathrm{R}([100-\mathrm{P}]/\mathrm{P})}$ where P=original % of the lighter component, P′=weighted % of the lighter component, R=weighting ratio W_H/W_L, where W_L=weighting of the lighter component (mol. wt. *d*, etc.), W_H weighting of the heavier component (mol. wt. *d*, etc.).

The formula for calculating molal per cent. is $P_M=\frac{100}{1+R([100-P_W]/P_W)}$ where P_M=molal % of the component of lower mol. wt. ; P_H=molal % of the component of higher mol. wt. ; P_W=weight % of the component of lower mol. wt. ; M_L=mol. wt. of preceding component ; M_H=mol. wt. of component of higher mol. wt. ; R=weighting ratio=M_L/M_H. Example : Component A, wt. % 20, mol. wt. 18 ; component B, wt. % 80, mol. wt. 32 ; then molal % A

$$=P_M=\frac{100}{1+18/32\times 80/20}$$

$$=30{\cdot}8 P_H=100-30{\cdot}8.$$

Volume % is derived from weight % by the following formula :

$$P_V=\frac{100}{1+R([100-P_W]/P_W)}.$$

P_V=volume % of lighter fraction, P_W=weight % of lighter fraction, D_L=density or specific gravity of lighter fraction, D_H=density or specific gravity of heavier fraction, R=D_L/D_H. Molal per cent. is calculated from volume per cent. by substituting P'_M for P′, P'_V for P, and R′ for R in the general formula ; here P'_V=volume % of lower ratio fraction, P'_M=molal % of lower ratio-fraction, and $R'=M_L\times D_H/(D_L\times M_H)$, the letters L and H referring to the fraction having the lower, L, or higher, H, ratio of mol. wt. to density M/D.

The calculation of the atomic percentages of two components of an alloy is discussed by Desch (*v.* Bibliography, *op. cit.* 14). If *a* and *b* are the atomic weights, *p* the percentage of the element of atomic weight *a*, and *x* its atomic percentage, $x/100-x=a/b\times p/100-p$. For these calculations, C. S. Smith (Amer. Inst. Min. Met. Eng. 1933, Contribution 60) has published tables of log $x/100-x$ and of log a/b. The equation is $x=100p/(p+a/b)(100-p)$; *cf.* P_M *supra.*

The graphs published by E. Nickel (Z. physikal. Chem. 1892, **10**, 450, 621) include a chart showing the connection between the percentage composition and the molecular composition of soda-lime glasses of the general formula $m\text{Na}_2\text{O}+n\text{CaO}+p\text{SiO}_2$. He writes

$$m62 : n56 : p60=x\%\text{Na}_2\text{O} : y\%\text{CaO} : z\%\text{SiO}_2,$$

and $n=1$ since relative values only are required ; then $m62/x=56/y=p60/z$ and $x+y+z=100$. The graph has $\text{Na}_2\text{O}\%$ as ordinates and CaO% as abscissæ and radial lines are drawn from 0 marked with molecular proportions of CaO and Na_2O. The disadvantage of the graph is that for practical use it must be drawn on a large scale. The same criticism applies to Nickel's graph of percentage and atomic composition of a number of aliphatic carbon compounds.

Triangular Charts are used for representing the percentages of the three components of a ternary mixture or alloy.

Each side of the equilateral triangle is considered to be divided into 100 equal parts and lines are drawn through each actual 10th division parallel to the sides. The three vertices A, B, and C represent the pure substances or 100% of A, B, and C respectively. Points on a side indicate the composition of binary mixtures ; any point within the triangle corresponds to a mixture of three substances. The point *m* on the side AB shows a mixture of 90% B and 10% A. The point X represents the mixture containing 23% A, 15% B, and 62% C. The preparation of such charts is greatly simplified by the use of specially ruled paper.

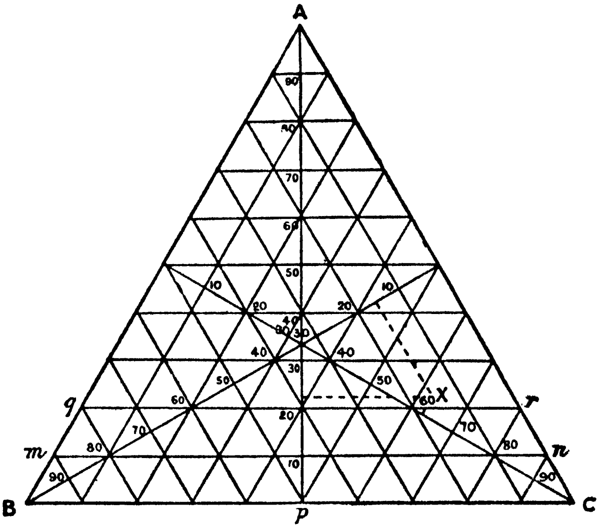


FIG. 1.

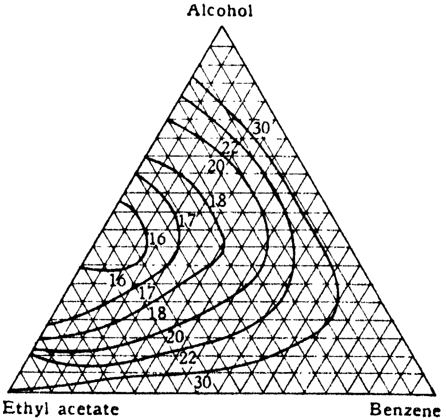


FIG. 2.

Cochrane and Leeper (J.S.C.I. 1927, **46**, 118T) in their study of the relative viscosities of nitrocellulose solutions in mixtures of three solvents used triangular graphs to record the composition of the mixtures, and as shown in Fig. 2 drew lines on the graph joining points corresponding to mixtures possessing the same relative viscosity. The graph shows clearly the effect of alcohol and of benzene in mixtures containing ethyl acetate as the third constituent.

W. Hume-Rothery (J. Inst. Metals, No. 2, 1933, **52**, 131 ; C. H. Desch, *v.* Bibliography) gives a graphical method of converting percentages by weight a, b, and c, of three elements, into atomic percentages, the atomic weights being w_a, w_b, and w_c.

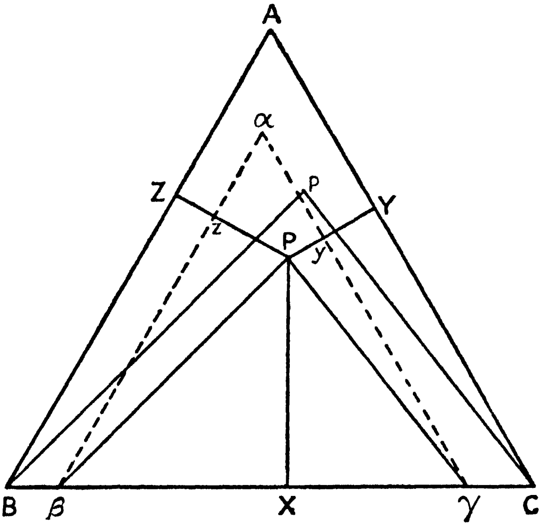


FIG. 3.

(Reproduced by permission of the Institute of Metals.)

The relative numbers of atoms are

$$a/w_a : b/w_b : c/w_c \quad . \quad . \quad . \quad . \quad (1)$$

whence

$$a/w_a \times w_a : b/w_b \times w_a : c/w_c \times w_a \quad . \quad . \quad (2)$$

or $$a \times 1 : b \times w_a/w_b = \mathrm{B} : c \times w_a/w_c = \mathrm{C} \quad . \quad (3)$$

The atomic percentages of the three elements are obtained by dividing 100a, 100B, and 100C, in each case by

$$a + \mathrm{B} + \mathrm{C} \quad . \quad . \quad . \quad . \quad (4)$$

In the graphical method, with 60° triangular ruled paper, the percentage composition of the alloy is represented by the point P in the equilateral triangle ABC of height 100 units. The weight percentages of A, B, and C are given by PX=a units, PY=b units, and PZ=c units (*cf.* Fig. 1). In accordance with equation (3) the points y in PY and z in PZ are then marked so that $Py = PY \times w_a/w_b$, and $Pz = PZ \times w_a/w_c$. Through y and z lines drawn parallel to AC and AB respectively form the equilateral triangle $\alpha\beta\gamma$. In this triangle the position of the point P corresponds to the atomic composition, since PX, Py, and Pz are in the ratio of equation (3); measurement of these lengths enables the calculation (4) to be carried out. These operations may be avoided by finding a new point p within the triangle ABC geometrically similar to P in the triangle $\alpha\beta\gamma$. This point is found by drawing through B and C lines parallel to βP and γP respectively which meet at p. The atomic composition is given by the position of the point p relative to the triangle ABC.

Graphic Representation by Two Adjacent Scales.—The familiar example is a thermometer graduated in Fahrenheit and Centigrade scales. Double scales are easily constructed from an ordinary graph, *e.g.* from the curve connecting the vapour tension of water (abscissæ) with the temperature (ordinates). The values of vapour tension for each degree Centigrade are read off and marked on the right hand side of the temperature axis, where they form an unevenly divided scale. Such a scale 22 cm. long for temperatures from 5° to 26°, and pressures from 7 mm. to 25·4 mm., graduated to 0·2°C. and 0·2 mm. is sufficiently accurate for ordinary purposes.

Nomograms (*v.* Bibliography).—In many cases an equation is solved by drawing three (or more) vertical axes graduated with appropriate numerical or logarithmic scales. In use a ruler is placed on the diagram to join observed values on the marginal scales; the imaginary line intersects the third axis at a point on its scale giving directly the required percentage, volume, etc. The accuracy obtained is about that of a slide rule for an axis of the same length but may be increased as required by drawing a portion of the graph on a larger scale.

Useful charts have been designed by H. G. Deming (Ind. Eng. Chem. 1916, **8**, 264 ; *v. also* Bibliography); of these Figs. 4 and 5 have been selected. Fig. 4 is a chart for the conversion of a given weight of one substance to the equivalent weights of a number of others ; it solves the equation $y=ax$ for different values of a. The ordinate scale on the left-hand margin

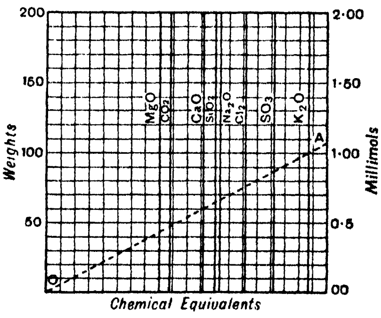


FIG. 4.

reads 1 cm.=1 mg., and on the right, 1 cm.=10 millimols. Along the horizontal axis measured distances in cm. from 0 are equal to one-fifth of the molecular weight of the compounds; from the points thus located, vertical axes are drawn marked with the formulæ, *e.g.* the CaO axis is placed 1/5×56·0=11·2 cm. from 0. To find the weight of $\mathrm{CO_2}$ equivalent to 100 mg. of $\mathrm{K_2O}$, a line is drawn from 0 through the point on the $\mathrm{K_2O}$ axis corresponding to 100 mg., which cuts the $\mathrm{CO_2}$ axis at 47 mg., which is the required equivalent weight. The same line cuts the right hand ordinate at 1·06 millimols., which is the molecular equivalent of 100 mg. $\mathrm{K_2O}$ and of 47 mg. $\mathrm{CO_2}$.

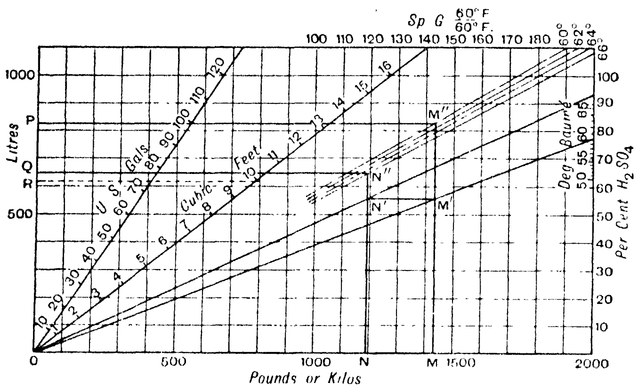


FIG. 5.

At 22·4 cm. from 0 a perpendicular axis may be drawn graduated with a scale 1 cm.=2 litres. If the left hand axis is read in g. of gases it will be seen that g. mols. lie on a line joining 0 and 22·4 L. on the volume axis. Volumes corresponding to other weights are read off, by joining 0 with the weights on the ordinate of each gas and observing the intercept on the volume axis. If the left-hand axis is read not in g. but in oz. avoirdupois, the readings on the volume axis are in cubic feet. This conversion follows from the fact that 1 oz. av.=28·35 g. and 1 cu. ft.=28·31 litres; 22·4×28·35/28·31, or 22·4 cu. ft. is the volume at N.T.P. of the molecular weight in oz. av.

The above chart (Fig. 5) has been drawn with special reference to the specific gravity and degree Baumé of strong sulphuric acid.

In this chart (Fig. 5) the horizontal axis is graduated in lb. or kg., the left hand vertical axis in litres and the perpendicular at the right hand margin in %$\mathrm{H_2SO_4}$ and degrees Bé. To find the weight of acid of 66°Bé. corresponding to 1,430 lb. of acid of 60°Bé., draw lines through 0 to the points corresponding to 60° and 66°Bé. From the point M corresponding to 1,430 lb. rule a vertical line to the 60°Bé. line at M′, thence a horizontal line which cuts the 66°Bé. line at N′, the abscissa of this point N=1,190 lb. of 66°Bé. The original paper should be consulted for other uses of the chart.

Charts showing the proportions required of two solutions to form a mixture of specified intermediate composition have been published. The graph (Fig. 6) was drawn by Hofmann and Reid (Ind. Eng. Chem. 1928, **20**, 436) to meet the requirements of the lacquer industry, *e.g.* 100 gallons of a batch weighing 10½ lb. per gallon is to be diluted with a solvent weighing 7½ lb. per gallon so that the mixture weighs 9½ lb. per gallon. A line is drawn connecting the two vertical scales at the points 9½. A perpendicular is drawn to the left hand scale at the point 10½ which intersects the diagonal line at a point from which a perpendicular to the horizontal axis indicates the volume of solvent required. Mixture-charts have been published by Wa. Ostwald (Chem.-Ztg. 1920, **44**, 241), J. S. Baker *et al.* (Ind. Eng. Chem. 1934, **26**, 910) and by O. Liesche (Chem. Fabr. 1928, **1**, 314), and Verlag Chemie, Berlin.

Water Softening.—The simple calculations required for ascertaining the correct quantities of lime and soda ash have been reduced to a parallel scale chart with 7 axes by Stratton, Ficklen, and Hough (Ind. Eng. Chem. 1932, **24**, 180). The radial chart for the same purpose published by A. Sulfrian (Chem.-Ztg. 1931, **55**, 209) is overburdened with details.

Mixed Acids. Nitration Acids.—Four triangular graphs for calculating the proportions of waste acid, nitric acid, and sulphuric acid have been drawn by E. Berl and his collaborators and published by J. Springer, Berlin. Dejmek (Physikal. Z. 1928, **29**, 907) discusses a logarithmic mixture law applicable to the conductivities of binary alloys, $\mathrm{Cd{-}Bi}$, $\mathrm{Ag{-}Pb}$, and also to the viscosity of liquid mixtures. Hofmann and Reid (*l.c.*) have drawn a radial nomogram (Fig. 7) for calculating the viscosity of a mixture of two liquids based on the approximation that the fluidities, *i.e.* the reciprocals of the viscosity, are additive.

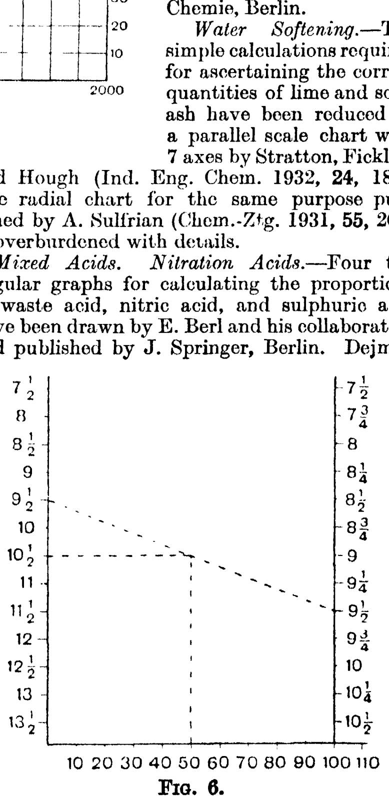


FIG. 6.

To ascertain the composition of a mixture with the viscosity 3 poises to be prepared by mixing two liquids (cellulose lacquers) of viscosities 2 and 4 respectively, a straight edge is placed on the chart connecting the points 2 and 4 on the marginal scales, the intersection on the line marked 3 gives the proportion 33·3% for the 2 poise lacquer.

Nomograms in Chemical Analysis.—**Zn/ZnO.** St. Reiner (Z. anal. Chem. 1926, **69**, 377) describes in detail the construction of a nomogram of three vertical axes; readings on the two exterior scales represent the weight of sample and the weight of zinc oxide respectively, these figures if joined by a black thread or a line on a celluloid ruler show the percentage figure of zinc on the interior axis. The construction of radial charts of the type of Fig. 7 is also described by this author.

$S/BaSO_4$.—A similar nomogram reading S% on the interior axis was published by O. Liesche (Chem. Fabr. 1928, **1**, 161), this graph is drawn advisedly for narrow limits of the weight of sample, and of barium sulphate, enabling 0·1% to be read between 36% and 44%.

The paper contains an interesting comparison with a chart for the same purpose plotted on rectangular co-ordinates.

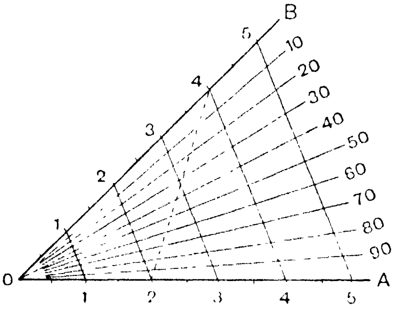


FIG. 7.

Sb_2S_3 and **Sb_2S_5** *from* **S** *and* **Sb** *found.*—The diagram replaces calculations in the rubber industry (*ibid.* 463).

Saponification Values.—A chart in which this number can be read directly is contained in "Rechenverfahren," 165 (*v.* Bibliography).

Reaction Velocity.—O. Liesche (*ibid.* 392, 621, 583) has constructed nomograms in the order given, for the relation between the velocity of a chemical reaction and the temperature (chloracetic acid → glycollic acid), the velocity of a monomolecular and of a bimolecular reaction.

Dry Weight % from Wet Weight %.—The chart by the same author (*ibid.* 377) for this conversion avoids a constantly recurring calculation in agricultural analysis.

Reduction of Gas Volumes.—Several authors have constructed nomograms for the reduction of observed volumes of gas to N.T.P. Höfsass (J. f. Gasbeleuchtung, 1916, **58**, 49) published a diagram which is unfavourably compared by Wa. Ostwald (Angew. Chem. 1919, **32**, 359) with his own chart on which the parallel axes for pressure and the reduction factor are divided logarithmically. This arrangement is criticised by Schwerdt and Loebe (Chem.-Ztg. 1920, **44**, 218), who divide the corresponding axes on their chart with a regular scale and as a useful addition give 2 double scales for reducing to 0°C. barometer readings on glass and brass scales respectively. Their temperature scale is curved on account of the correction for vapour tension (*v.* Barr, *infra*). Deming (*l.c.*) like Ostwald employs logarithmic scales, but his chart is too small for practical use. Liesche (*l.c.* 622) supplies a chart with particulars of the method of construction. F is the sloping axis of correction factors, its scale is projected from the 15° point of the $t°$ axis on the left margin, through an evenly divided auxiliary scale. The pressure axis on the right margin is graduated downwards from 700 mm. to 800 mm. The $t°$ axis is graduated upwards from 5° to 25°. The upper limit of the F scale F_a reads 0·8437, the lower limit F_e 1·0336. F_a has abscissa $x_{F_a} = 136{\cdot}1$ mm., F_e has abscissa 127·0 mm. Distance of a point F of the F scale from F_a in 1569 F mm-

$$= (1569F - 1400)/(0{\cdot}5566F + 1)$$

Key equation $x_F/(y_F - y_p) = 200/(y_t - y_p)$.

$$F = 0{\cdot}3593p/(273{\cdot}1 + t).$$

p Scale, $x_p = 200$ mm. $y_p = (800 - p) \times 2$ mm.

t Scale, $x_t = 0$ mm. $y_t = (t - 5) \times 10$ mm.

F scale, $x_F = 200/(0{\cdot}5556F + 1)$.

$$y_F = (1600 - 1548F)/(0{\cdot}5566F + 1).$$

The length of axes in this chart is about 6·6 cm. A chart for higher temperatures, 200°–1,000°, and pressures 10–200 atmospheres has been constructed (Liesche, *ibid.* 595).

R. C. Farmer published a "gas calculator," a nomogram for the correction of volumes of wet and dry gas and also for the logarithm of the weight of 1 c.c. if the gas measured is nitrogen (Baird and Tatlock, London, out of print). Berl and collaborators (*v.* Bibliography) have drawn a nomogram for correcting the volumes of wet or dry gases. The reduction factor ranges from 0·790 to 1·000 on an axis 21·8 cm. long. Liesche's chart, published by Verlag Chemie (*v.* Bibliography), avoids the use of a separate axis for wet gases by correcting the volume of a wet gas, measured over water, by means of a vapour tension scale on one side of the temperature axis, which ranging from 5°–26° is 21 cm. long. There is also a double scale on the factor axis, the right hand side being graduated in mg. nitrogen. Both Berl's and Liesche's nomograms, except for their fragile nature, are well adapted for use in the laboratory.

The method of constructing a gas reduction nomogram is discussed by G. Barr, who has kindly given his consent to the reproduction of the figure (Fig. 8) and description in his publication (J.S.C.I. 1930, **49**, 21T). The following text except for two small verbal alterations introduced by Dr. Barr (private communication, 18/2/38) follows the paper cited.

If parallel logarithmic scales are used for B and f, the temperature scale is a straight line, divided proportionately to log $(1 + \alpha t)$, when the gas is dry; when the gas is wet three straight logarithmically divided scales cannot afford an exact solution owing to the impossibility of separating the variables B and p in the equation:

$$f=\frac{Vo}{V}=\frac{B-p}{760\,(1+at)}$$

Coste (Analyst, 1929, **54**, 656) avoids the difficulty by attaching to the chart a vapour-pressure curve so that p may be subtracted from B before performing the alignment. The equation for dry gases may also be solved by the use of a Z-chart, containing two parallel scales for pressure and temperature divided linearly, the diagonal being graduated to give the reduction factor (*cf.* Bibliography, Peddle, Ch. VIII). The adoption of linear scales facilitates the construction and increases the accuracy of interpolation. Such a chart has been described by Liesche (*l.c.* 1928, **1**, 621), embracing the range 5°–25°C. and 700–800 mm. pressure: a nomogram of this type cannot, however, be adapted to deal with moist gases owing to the form of the equation, which requires that the temperature scale be non-uniform and curved.

The nomogram illustrated in Fig. 8 has parallel linear scales for barometric pressure and for the conversion factor. When used for dry gases it differs from Liesche's only in the position and type of graduation of the temperature and factor scales. It possesses the important advantage, however, that the t scale may alternatively be so graduated as to refer to moist gases. The scales used in the range selected are:

For dry gases :

$$x=0 \qquad y=0{\cdot}5(B-725)$$

$$x=1 \qquad y=200(f-0{\cdot}865)$$

$$x=1+\frac{0{\cdot}52631}{0{\cdot}47368+at} \qquad y=\frac{17{\cdot}789-173at}{0{\cdot}47368+at}$$

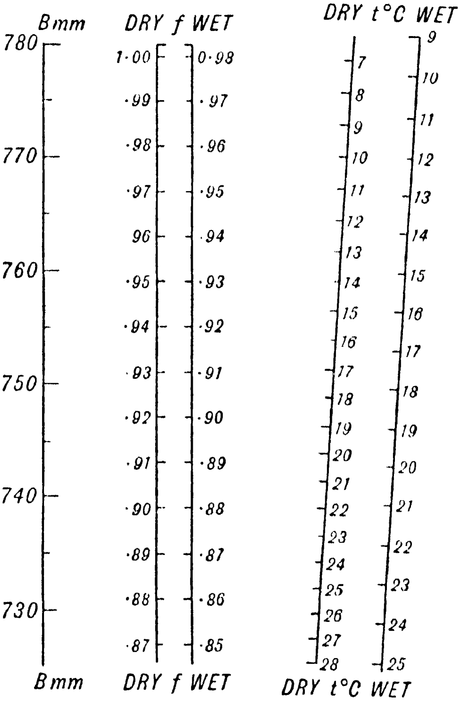
For wet gases :

$$x=0 \quad y=0{\cdot}5(B-725)$$

$$x=1 \quad y=200(f-0{\cdot}845)$$

$$\begin{cases} x=1+\dfrac{0{\cdot}52631}{0{\cdot}47368+at} \\[2ex] y=\dfrac{21{\cdot}789-169at-0{\cdot}26316p}{0{\cdot}47368+at} \end{cases}$$

The scale unit for x is independent of that for y; in the figure it has been taken as 12·5 and 14 times the y unit for the dry and wet scales respectively, the difference giving a reasonable separation of the axes. If a common factor scale is used for both conditions, the temperature scales are too close for convenience. The factor f for reduction to N.P.T. is the point of intersection on the f scale obtained by joining the barometric pressure on scale B to the temperature on the appropriate t° scale suffices for ordinary calculations being in fact greater than that with which the gas laws themselves hold. Using the average value 0·003669 for a, the following values of the co-ordinates for the temperature scales have been calculated.



$$f=\frac{V_{NTP}}{V}=\frac{B-p}{760(1+at)}$$

Fig. 8.

t°C.	y Dry.	y Saturated.	t°C.	y Dry.	y Saturated.
8	25·270	—	19	10·544	10·436
9	23·834	—	20	9·313	8·724
10	22·419	—	21	8·098	7·007
11	21·024	24·080	22	6·900	5·283
12	19·649	22·369	23	5·717	3·552
13	18·294	20·662	24	4·550	1·812
14	16·957	18·957	25	3·398	0·061
15	15·639	17·254	26	2·260	—
16	14·339	15·552	27	1·137	—
17	13·056	13·849	28	0·029	—
18	11·791	12·144	—	—	—

The values of x for either scale are given by :

t°C.	8	11	15	19	23	25	28
x	2·04627	2·02388	1·99545	1·96856	1·94310	1·93086	1·91308

The temperature scale for dry gases is a straight line, but that for wet gases is curved. The curvature is, however, very slight, and the five points indicated are ample to fix the position and shape of the curve. The sub-division of the *t* scale into 1/5°C. is most readily performed by projection.

Fig. 8 is, in reality, two nomograms, of which one scale (B) has been made identical. If the application of the diagram is to be confined to dry or to wet gases only, it may be convenient to add a uniformly divided horizontal scale, as described and figured in J.S.C.I., 1930, **49**, 22T, by means of which the multiplication of the factor may be effected.

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J. N. G.

CHEMICAL WARFARE.

Introduction.—Chemical warfare, also called gas warfare, may be defined as the use in war, for the purpose of injuring an adversary, of any substance within the realm of chemistry—whether gaseous, liquid, or solid—which is in any way harmful to the human or animal organism. Chemical warfare is prohibited by the Geneva Protocol of 1925, and the prohibition includes any lachrymatory, irritant, vesicant, asphyxiant, or poisonous substance, but excludes the normal use of recognised explosives and of products employed as screening smokes, which latter, under normal conditions of use, are not injurious to human beings.

Chemical warfare substances, which are often called poison gases or simply gas, generally produce their effect on the human body either when breathed in the form of vapour or finely divided particles, or by contact with the eyes or skin, whether in the form of vapour or liquid.

Physiological Classification.—Chemical warfare substances may be classified according to the chief effect which they exercise on the human body. They fall into the following three main groups, which depend solely on the part of the body mainly affected :

(1) Lung irritants, which attack the lungs and breathing passages. The severity of the effects depends upon the substance used. Some gases, such as chlorine and phosgene, will produce death if breathed in sufficiently high concentration, and are said to be lethal. On the other hand, substances such as the arsenicals, which are used in the form of clouds of finely divided particles (sometimes called toxic smokes) produce intense irritation of the breathing passages, but the effects, while painful, are usually only temporary, and pass off completely in an hour or two after leaving the contaminated atmosphere. This main group is sometimes divided into two classes, namely lethal gases, to include those which may cause death, such as chlorine and phosgene, and sensory irritants, to cover those which affect the breathing passages but are generally not lethal, like the arsenicals.

(2) Eye irritants (lachrymators, or tear gases). Even in very small amounts these have an immediate and painful effect, causing so profuse a flow of tears that it is generally very difficult, if not impossible, to see. The effects soon wear off and no damage is done to the eyes.

(3) Skin irritants (blistering gases, or vesicants). These substances, of which mustard gas is a typical example, attack the skin, and in the worst cases cause deep and extensive blisters. No pain is felt on contact with the liquid or the vapour, and the effects do not show themselves until after a few hours. Mustard gas also attacks the eyes and lungs, and here again there are no immediate symptoms. This constitutes one of the greatest dangers in dealing with mustard gas. There have been recent references to a new type of gas called a " prickling " gas. Such a substance, the main action of which is on the skin, would fall into the skin irritant class.

The above classification is of a very general nature, since most gases act on more than one part of the body. In fact, most war gases affect the eyes, whatever action they may have upon other parts of the body. The effects produced by any war gas depend on the concentration of the gas and the length of time a person is exposed to it. By concentration is meant the amount of gas in the atmosphere ; this is usually expressed as 1 vol. or part of the gas, assumed to be in the form of vapour, in a stated number of volumes or parts of air, or as so many milligrams of the gas in a litre of air. The higher the concentration, the shorter is the exposure required to produce death or injury. In the case of gases which injure the lungs, a man must, however, breathe a certain minimum quantity of the poison before it will do him any real harm, the amount of harm depending not only on the nature of the gas, but also on the concentration and the volume of air the man is breathing. If breathing vigorously, as when doing heavy work, a man will be affected by gas more quickly than if he were breathing quietly, as when resting. With rare exceptions all chemical warfare substances, even in low concentrations, will cause injury if inhaled for a sufficiently long period. With substances which are merely eye irritants, and with the toxic smoke arsenicals, there is usually a concentration below which an individual may be exposed to the gas for an unlimited period of time without suffering any ill effects. The concentrations of the more powerful gases of these types are very low, being of the order of one part of gas in a thousand million parts of air or even lower.

Military Classification.—From the point of view of gas defence and of military tactics, chemical warfare substances are generally divided into two main categories, namely :

(*a*) Non-persistent.
(*b*) Persistent.

When liberated, non-persistent substances are rapidly converted into clouds of gas or smoke, which continue to be effective until dissipated by the wind. They are generally liquids with a low boiling-point, or solids which are dispersed as a fine fume or smoke by heat or explosion. Typical examples are chlorine and phosgene and the arsenicals. Persistent gases generally consist of liquids of high boiling-point which evaporate slowly. On the burst of a shell or bomb containing them they contaminate the surrounding area on which they are scattered and continue to give off harmful vapours for a considerable period. Mustard gas and most tear gases are typical examples. There is naturally an intermediate class where the persistence is of limited duration. This class, of which diphosgene and chloropicrin are typical, is sometimes called semi-persistent. In practice, however, it is convenient to have only the two main classes and to indicate the degrees of persistence for those which are not in the non-persistent group. The boiling-point is a good indication as to whether a substance is persistent or non-persistent. With liquids the higher the boiling-point the greater the persistence, and *vice versa.*

Concentrations obtainable in the Field.—As a general rule, the concentrations of gas obtainable in the field may be regarded as low by normal standards, that is to say, it is unusual to get a concentration in excess of 1 part of gas in 100 parts of air. In practice, the concentration is generally very much lower, and will depend on the nature of the gas (*i.e.* whether persistent or non-persistent), the size and number of shells or bombs falling in the area, the nature of the area (*i.e.* whether open country, trenches, or built up), and the weather conditions (high winds cause low concentrations and *vice versa*). High concentrations are obtainable only with the non-persistent gases. The following figures, based on published data of a reliable nature, are typical of the average and maximum concentrations likely to be produced under favourable military conditions with a few representative gases :

Gas.	Type.	Average concentration.	Maximum concentration.
		1 part of gas in x parts of air.	
Phosgene	Non-persistent lethal lung irritant	1 in 2,000–4,000	1 in 30
Chloropicrin	Semi-persistent lethal lachrymator	Rather less than for phosgene owing to lower volatility	
Diphenylchloroarsine	Non-persistent lung irritant	1 in 500,000–1,000,000	1 in 250,000
Ethyl iodoacetate	Persistent lachrymator	1 in 20,000–40,000	1 in 8,000
ββ-dichlorodiethyl sulphide (mustard gas)	Persistent vesicant	1 in 350,000	1 in 200,000

These concentrations refer to the area on which the shell or bombs actually fall. The gas clouds will be diluted by the wind and the concentrations will fall off rapidly down wind from the point of burst of the shell or bomb. The maximum concentrations given are produced only under very favourable conditions.

The most modern and efficient types of gas mask will give complete protection for a considerable period against even the highest concentrations obtainable under service conditions.

Physiological Data.—The figures in the table at the top of p. 9 for a number of representative chemical warfare agents give a rough guide, from the defensive point of view, as to the minimum lethal and incapacitating concentrations of the gases mentioned for an unprotected man, and as to the minimum concentrations that can be breathed indefinitely without damage to the human organism.

In view of its special importance and of the fact that it can act on all parts of the body, it is more convenient to set out the physiological data for the action of the vapour of ββ-dichlorodiethyl sulphide (mustard gas) in the following manner :

PHYSIOLOGICAL ACTION OF MUSTARD GAS VAPOUR.

Concentration.	Periods of exposure to produce:				
	Slight eye effects.	Severe eye effects.	Mild skin effects.	Severe skin effects.	Lung injury.
1 in 100,000 .	—	3–5 mins.	—	2 hrs.	—
1 in 1 million .	10–15 mins.	1 hr.	1 hr.	—	1 hr.
1 in 2 million .	—	2hrs.	—	—	nil
1 in 5 million .	1½ hrs.	6 ,,	—	—	nil
1 in 10 million .	3 ,,	12 ,,	—	—	nil

The minimum concentration of mustard gas vapour normally detectable by smell is between 1 in 5,000,000 and 1 in 10,000,000.

***Medical Aspects.*—An account of the medical**

LETHAL AND INCAPACITATING CONCENTRATIONS FOR AN UNPROTECTED MAN.

	Effective concentration (*i.e.* concentration which will incapacitate) for unprotected men for exposures of:		Lethal concentration for unprotected men for exposure of:		Concentration which can be breathed indefinitely without damage.
	2 minutes.	10 minutes.	2 minutes.	10 minutes.	
Diphenyl chloroarsine	1:7·5 million	1:75 million	1:8,000	1:40,000	1:1,000 million
Diphenylamine chloroarsine	1:7·5 ,,	1:75 ,,	1:8,000	1:40,000	1:1,000 ,,
Diphenyl cyanoarsine	1:17 ,,	1:170 ,,	1:16,000	1:80,000	1:2,500 ,,
Ethyl iodoacetate. .	1:5 ,,	1:10 ,,	(1)	(1)	1:100 ,,
Chlorine	1:10,000	1:40,000	1:2,000	1:10,000	1:175,000
Phosgene	1:70,000	(2)	1:10,000	1:50,000	1:1 million
Chloropicrin . . .	1:100,000	1:200,000	1:4,000	1:20,000	1:1 ,,
Chloroacetophenone .	1:5 million	1:100 million	(1)	(1)	1:250 ,,
Bromobenzyl cyanide	1:10 ,,	1:25 ,,	(1)	(1)	1:250 ,,

(1) In practice a lethal concentration can hardly be obtained in the field with the lachrymators ethyl iodoacetate, chloroacetophenone, and bromobenzyl cyanide.

(2) A concentration of phosgene which is just insufficient to cause immediate coughing or lachrymation can usually be tolerated, since the initial irritation tends to subside. Such an atmosphere is extremely dangerous, as continued inhalation may end fatally.

aspects of chemical warfare agents is outside the scope of the present article, but the bibliography (p. 17) contains a list of the more important publications on the subject. For most purposes the "Manual of Treatment of Gas Casualties," issued by the War Office and obtainable from H.M. Stationery Office, will be found adequate.

Methods of Use.—Chemical warfare, in the now accepted sense, started with the liberation of chlorine from cylinders by the Germans in 1915. Subsequently other noxious substances were used in shell, trench-mortar bombs, and grenades, and as experience developed, the shell—by which is meant the artillery shell—became the chief weapon for the use of chemical warfare agents. The use of gas in artillery shell was practically confined to shell of calibre of 6 in. and under, the most effective calibres being between 4 in. and 6 in. The artillery shell suffers from the defect that the ratio of weight of gas contained in it to the total weight of the shell is low unless thin walled shells made of steel of high tensile strength are used. The quantities of gas contained in typical war shells were approximately as follows in the case of phosgene and mustard gas:

Calibre.	Weight of gas.	% Ratio of weight of gas to total weight of shell.
	lb.	
3 in. (75 mm. and 18 pdr.) . .	1·3	6
4·5 in. (105 mm.)	4·25	10
6 in. (150 mm.) .	11·0	11

In the normal gas shell, an air space of about 10% was allowed, to permit of the expansion of the contents with heat. There was a small bursting charge in the head of the shell just sufficient to break it open and distribute the contents effectively. A percussion fuse was employed. Towards the end of the war the Germans introduced the use of a mustard gas shell with a big explosive charge to produce very fine atomisation of the contents, thus dissipating the gas in a highly toxic cloud but reducing the amount of liquid scattered on the ground and thus decreasing the persistence. For solid arsenicals like diphenylchloroarsine and diphenylcyanoarsine the Germans employed a shell in which the toxic material contained in a bottle was embedded in high explosive. This shell (called blue cross) was practically a double purpose shell, as it had considerable explosive value as well as liberating a toxic cloud, or smoke, of finely divided particles of the arsenical.

Trench mortar bombs of 3 in. and 4 in. calibre were also used with effect, but they suffered from the disadvantage of short range. For the gas bombardment of an important area the most effective weapon was the Livens projector, a crude mortar with no great accuracy and limited range, but which had the advantage that large numbers, running into thousands, could be fired simultaneously. The bomb or drum contained a large amount of gas (about 30 lb.) and the ratio of gas content to total weight was high (about 46%). The gas generally used was phosgene. A very heavy concentration could be put down at once over an area and the concentration was so high that troops taken by surprise were killed or disabled before they could put on their gas masks.

At the end of the war a new development was being initiated for the liberation of poisonous or irritant smokes by the volatilisation by means of heat of solid arsenicals in stationary appliances generally known as generators. An important object in using such smokes was to penetrate the gas mask and cause the wearer to remove it and so expose himself to the action of lethal gases used at the same time. The degree of penetration obtainable depends on the size of the particles in the smoke ; the smaller the particle the greater is the penetration, but since the actual quantity of material passing through the mask is what matters from the point of view of the subsequent physiological effect on the wearer, the result is that for each type of mask there is a particular size or range of sizes giving the best practical results. This represents the condition which gives the maximum amount of toxic material actually reaching the wearer.

The use of gas in aircraft bombs was subsequent to the Great War a fully authenticated case being the employment of mustard gas in air bombs by the Italians in the Abyssinian campaign in 1935–36. Air bombs can have quite thin walls and the percentage ratio of weight of gas to total weight may be 50 and over, thus showing a very high efficiency as compared with the shell. The post-war period has also seen developments for the use of liquids by spraying from aircraft (also employed with mustard gas in the Abyssinian campaign) or in other ways involving discharge under pressure or into heated pipes, such as engine exhausts.

Main Characteristics.—The table (pp. 12–15) gives the main characteristics of all the chemical warfare agents which have been used. The term " trench-mortar bombs " refers to all short-range weapons, of which the Livens projector was a particularly effective type. The term " grenade " refers to bombs for throwing by hand. The symbols used in the table have the following significance :

Lach. = Lachrymatory
Leth. = Lethal
L.I. = Lung irritant
V. = Vesicant
N.I. = Not important
T.M. = Trench mortar

While many substances were used by themselves for offensive purposes, others such as prussic acid were employed only in admixture with other materials in order to obtain their maximum efficiency. Other mixtures were used when it was desired to produce more than one effect at the same time ; for example, a mixture of trichloromethyl chloroformate, phosgene, and diphenylchloroarsine was used by the Germans to get a moderately persistent lethal effect in conjunction with the highly irritant but non-lethal action of the arsenical; a further intention was to bring about the penetration of the gas masks of the period, which were comparatively poor in their protection against an arsenical toxic smoke, thus causing the wearer to remove the mask because of the irritant action on his breathing passages and so expose himself to the toxic action of the other two constituents. Such double purpose mixtures are now generally regarded as of doubtful utility. The main mixtures are set out below. Where the compositions were approximately constant the percentage of each constituent by weight is indicated in brackets.

Bromoacetone (80%) and chloroacetone (20%).
Chlorine (50%) and phosgene (50%).
Chlorine (70%) and chloropicrin (30%).
Chloropicrin (65%) and hydrogen sulphide (35%).
Chloropicrin (80%) and stannic chloride (20%).
Chloropicrin (75%) and phosgene (25%).
Cyanogen bromide with bromoacetone or bromomethyl ethyl ketone.
$\beta\beta$-Dichlorodiethyl sulphide (80%) and either chlorobenzene or carbon tetrachloride (20%).
Dimethylsulphate (75%) and methyl chlorosulphonate (25%).
Diphenylcyanoarsine (50%) and ethylcarbazole (50%).
Ethyldichloroarsine (80%) and dichloromethyl ether (20%).
Ethyldichloroarsine, ethyldibromoarsine, and dichloromethyl ether, sometimes with methyldibromoarsine.
Ethyl iodoacetate (75%) and alcohol (25%).
Hydrocyanic acid (55%), chloroform (25%), and arsenic trichloride (20%).
Hydrocyanic acid (50%), arsenic trichloride (30%), stannic chloride (15%), and chloroform (5%).
Phosgene (50%) and arsenic trichloride (50%).
Phosgene (60%) and stannic chloride (40%).
Trichloromethyl chloroformate (65%) and chloropicrin (35%).
Trichloromethyl chloroformate, phosgene, and diphenylchloroarsine.
Xylyl bromide and bromoketone or benzyl bromide.

In the table on p. 16 are shown a few important chemical warfare agents which have not been used in actual warfare.

Outline of Methods of Manufacture.

1. Acrolein : by distillation of glycerol ($CH_2(OH)CH(OH)CH_2{\cdot}OH$) with potassium hydrogen sulphate ($KHSO_4$) or magnesium sulphate ($MgSO_4$).

2. Allyl *iso*thiocyanate : from natural sources, and by distillation of allyl bromide

$$(CH_2{:}CH{\cdot}CH_2Br)$$

or iodide with alcoholic potassium thiocyanate ($KCNS$) or silver thiocyanate ($AgCNS$).

3. Arsenic trichloride : by the action of hydrogen chloride on arsenious oxide (As_2O_3).

4. Benzyl bromide : by the bromination of toluene ($C_6H_5{\cdot}CH_3$).

5. Benzyl chloride : by the chlorination of toluene ($C_6H_5{\cdot}CH_3$).

6. Benzyl iodide : by interaction of benzyl chloride (*q.v.*) in alcoholic solution, with sodium or potassium iodide (NaI or KI).

7. Bromine : from metallic bromides by the action of chlorine, or of sulphuric acid and an oxidising agent.

8. Bromoacetone : by the bromination of acetone ($CH_3{\cdot}CO{\cdot}CH_3$) by gaseous or liquid bromine.

9. Bromobenzylcyanide : by the conversion of benzyl chloride (*q.v.*) to benzyl cyanide ($C_6H_5{\cdot}CH_2{\cdot}CN$) by treatment with sodium cyanide ($NaCN$) with subsequent bromination.

10. Bromomethyl ethyl ketone : as for bromoacetone, using methyl ethyl ketone

$$(CH_3{\cdot}CO{\cdot}C_2H_5)$$

instead of acetone.

11. Carbon tetrachloride : by direct chlorination of carbon disulphide (CS_2) in the presence of a catalyst.

12. Chlorine : by the electrolysis of brine (sodium chloride ($NaCl$) solution).

13. Chloroacetone : by the chlorination of acetone ($CH_3{\cdot}CO{\cdot}CH_3$).

14. Chloroacetophenone : by the chlorination of acetic acid ($CH_3{\cdot}COOH$) and its subsequent conversion to chloroacetylchloride ($CH_2Cl{\cdot}COCl$) by treatment with thionyl chloride ($SOCl_2$). The chloroacetylchloride is then condensed with benzene (C_6H_6) by the Friedel and Craft reaction in the presence of aluminium chloride to give the desired product.

15. Chlorobenzene : by the chlorination of benzene (C_6H_6).

16. Chloroform: from acetone ($CH_3{\cdot}CO{\cdot}CH_3$) by the action of bleaching powder.

17. Chloropicrin : by the action of bleaching powder or chlorine on picric acid

$$(C_6H_2(NO_2)_3OH).$$

18. Chlorosulphonic acid : by the saturation of oleum (SO_3) with hydrogen chloride and subsequent distillation.

19. Chlorovinyldichloroarsine : by the interaction of acetylene (C_2H_2) and arsenic trichloride (*q.v.*) in the presence of aluminium chloride (Al_2Cl_6) with subsequent fractional distillation under reduced pressure and treatment to convert the higher homologues, namely dichlorodivinylchloroarsine and trichlorotrivinylarsine into the product desired.

20. Cyanogen bromide : from the interaction of potassium cyanide (KCN) in aqueous solution and bromine at low temperature.

21. Cyanogen chloride : by chlorination of hydrocyanic acid (HCN) in aqueous solution.

22. Dichlorodiethylsulphide : three methods:

(*a*) By the conversion of ethylene (C_2H_4) obtained by dehydrating alcohol vapour ($C_2H_5{\cdot}OH$) over a phosphoric acid or other suitable catalyst into chlorohydrin ($CH_2(OH)CH_2Cl$) by hypochlorous acid ; the chlorohydrin is treated with sodium sulphide (Na_2S) to give thiodiglycol [$(C_2H_4{\cdot}OH)_2S$] which, on treatment with hydrochloric acid or thionyl chloride ($SOCl_2$) yields dichlorodiethyl sulphide.

(*b*) By the interaction of ethylene and sulphur dichloride (SCl_2) with or without a solvent.

(*c*) By the interaction of ethylene and sulphur monochloride (S_2Cl_2) with or without separation of the liberated sulphur.

23. Dichloromethyl chloroformate : by the regulated chlorination of methyl formate ($H{\cdot}COOCH_3$).

24. Dichloromethyl ether : by the action of phosphorus trichloride (PCl_3) on trioxymethylene [$(CH_2O)_3$] in the presence of zinc chloride ($ZnCl_2$).

25. Dimethyl sulphate : by the interaction of methyl alcohol ($CH_3{\cdot}OH$) and chlorosulphonic acid (*q.v.*).

26. Diphenylamine arsenious chloride : by the interaction of diphenylamine [$(C_6H_4)_2NH$] and arsenic trichloride (*q.v.*).

27. Diphenylchloroarsine : three methods :

(*a*) By the production of triphenylarsine [$(C_6H_5)_3As$] by the interaction of chlorobenzene (C_6H_5Cl) and arsenic trichloride (*q.v.*) in the presence of sodium and its subsequent treatment with arsenic trichloride.

(*b*) By the diazotisation of aniline ($C_6H_5{\cdot}NH_2$) and subsequent treatment with sodium arsenite (Na_2HAsO_3) to give phenylarsonic acid ($C_6H_5{\cdot}AsO_3H_2$). The acid is reduced by sulphur dioxide (SO_2) to phenylarsinic acid ($C_6H_5{\cdot}AsO_2H)_2$, which on treatment with a further amount of diazotised aniline gives diphenylarsonic acid [$C_6H_5{\cdot}AsO_2H$]. This acid on reduction to diphenyl arsenoxide [$(Ph_2As)_2O$] and treatment with hydrochloric acid yields the product desired [$(C_6H_5)_2AsCl$].

(*c*) By the reduction of phenylarsonic acid obtained as in (*b*) partly to phenylarsenious oxide ($C_6H_5{\cdot}AsO$) and partly to phenyldichloroarsine ($C_6H_5AsCl_2$), so that the resulting mixture when heated in an autoclave will be converted into the product desired.

28. Diphenylcyanoarsine : by the treatment of diphenylchloroarsine (*q.v.*) with sodium cyanide ($NaCN$) or anhydrous hydrocyanic acid (HCN).

29. Ethylcarbazole : by the interaction of carbazole ($C_{12}H_9N$) and ethyl sulphate [$(C_2H_5)_2SO_4$].

30. Ethyldibromoarsine : by the interaction of magnesium ethyl iodide (MgC_2H_5I) with potassium arsenite (K_2HAsO_3) to give magnesium ethyl arsenite [$Mg(C_2H_5)AsO_3$] which is then reduced by sulphur dioxide in hydrobromic acid solution.

31. Ethyldichloroarsine : as for methyldichloroarsine, using ethyl sulphate in place of methyl sulphate or by treatment of ethyl chloride (C_2H_5Cl) with sodium arsenite (Na_2HAsO_3) and the reduction of the ethyl arsonic acid ($C_2H_5{\cdot}AsO_3H_2$) by sulphur dioxide to ethyl arsenious oxide ($C_2H_5{\cdot}AsO$), which gives on treatment with hydrochloric acid the desired product.

32. Ethyliodoacetate : by the chlorination of acetic acid ($CH_3{\cdot}COOH$) and subsequent esterification to give ethyl chloroacetate ($CH_2Cl{\cdot}COOC_2H_5$), which is then treated with sodium iodide (NaI).

33. Hydrocyanic acid : by the action of acid on metallic cyanides.

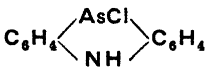
34. Hydrogen sulphide : by the action of acid on metallic sulphides.

35. Iodoacetone : by the action of potassium iodide (KI) on chloroacetone (*q.v.*).

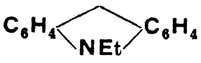
36. Methyl chloroformate : by the regulated chlorination of methyl formate ($H{\cdot}COOCH_3$).

List of Chemicals which have been used in Warfare and their Characteristics.

1. Chemical name.	2. Formula.	3. Physical characteristics. °C.	4. Physiological action.	5. Method of use.	6. Neutralising agent.	7. Remarks.
Acrolein (Allyl or acraldehyde).	$CH_2{:}CH{\cdot}CHO$	M.p. −88 B.p. 52	Lach. L.I.	Grenades and shell.	—	N.I.
Allyl *iso*thiocyanate .	$CH_2{:}CH{\cdot}CH_2{\cdot}NCS$	B.p. 151	Lach. Leth. V.	—	—	Found in small amounts in shell. Not used by itself.
Arsenic trichloride (Arsenious chloride).	$AsCl_3$	M.p. −18 B.p. 130	No special action.	Used in mixtures with hydrocyanic acid and phosgene.	Alkalis.	—
Benzyl bromide . . .	$C_6H_5{\cdot}CH_2Br$	M.p. −3·9 B.p. 198	Lach.	Shell, often in admixture with xylyl bromide.	Sulphur in soda solution.	N.I.
Benzyl chloride . . .	$C_5H_5{\cdot}CH_2Cl$	B.p. 179	Lach.	Shell.	Ditto.	N.I.
Benzyl iodide . . .	$C_6H_5{\cdot}CH_2I$	M.p. 24 (decomposes on distillation)	Lach.	Shell.	Ditto.	N.I.
Bromine	Br_2	M.p. −7·3 B.p. 58·8	Leth. L.I.	Grenades.	Alkali or sodium thiosulphate.	N.I.
Bromoacetone . . .	$CH_3{\cdot}CO{\cdot}CH_2Br$	M.p. −54 B.p. 136 at 725 mm.	Lach. L.I.	Shell, with or without chloroacetone or cyanogen bromide.	(*a*) Sodium hypobromite and sodium carbonate solution. (*b*) Alkalis.	Fairly important.
Bromobenzyl cyanide .	$C_6H_5{\cdot}CHBr{\cdot}CN$	M.p. 29 B.p. 231·7	Lach.	Shell.	Alkalis.	Powerful tear gas.
(" Bromoketone ") . . Methyl *a*-bromoethyl ketone *or*	$CH_3{\cdot}CO{\cdot}CHBr{\cdot}CH_3$ *or*	B.p. 133–134	Lach. L.I.	Shell and grenades. Sometimes with xylyl bromide or cyanogen bromide.	—	N.I.
Bromomethyl ethyl ketone.	$CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	B.p. 145–146				
Carbon tetrachloride .	CCl_4	B.p. 76·8	No special action.	As diluent for mustard gas.	—	—
Chlorine	Cl_2	M.p. −102 B.p. −34·6	Leth. L.I.	Cylinders : by itself or mixed with phosgene or chloropicrin.	Sodium hyposulphite (thiosulphate).	First gas used.
Chloroacetone . . .	$CH_3{\cdot}CO{\cdot}CH_2Cl$	B.p. 119	Lach.	Shell with bromoacetone.	As for bromoacetone.	N.I.

Chlorobenzene	C_6H_5Cl	B.p. 132	No special action.	As diluent for mustard gas.	—	—
Chloroform	$CHCl_3$	B.p. 61·2	No special action.	In mixture with hydrocyanic acid.	—	N.I.
Chloropicrin	$CCl_3{\cdot}NO_2$	M.p. −69 B.p. 112	Leth. Lach.	Shell and T.M. bombs in admixture with stannic chloride, phosgene or trichloromethyl chloroformate; in cylinders with hydrogen sulphide or chlorine.	Sodium sulphide.	Cumulative in its action.
Chlorosulphonic acid	$SO_2Cl{\cdot}OH$	B.p. 155	No special action.	Grenades and T.M. bombs.	Alkalis.	Main value is as a screening smoke.
Cyanogen bromide	$CNBr$	M.p. 52 B.p. 61·3	L.I.	Shell, sometimes with bromoacetone or bromomethyl ethyl ketone	Alkalis.	N.I.
Cyanogen chloride	$CNCl$	M.p. −6 B.p. 15·5	L.I. Lach.	Shell.	Ditto.	—
ββ′-Dichlorodiethyl sulphide (mustard gas).	$(CH_2Cl{\cdot}CH_2)_2S$	M.p. 14·4 B.p. 217–219	V. L.I. Leth.	Shell in admixture with carbon tetrachloride or chlorobenzene as diluents.	Bleaching powder, sodium hypochlorite or other chlorinating agents.	Powerful war gas; attacks all parts of the body with which it comes in contact, whether as vapour or liquid; effect very marked on eyes. Very insidious. No immediate symptoms; effects develop in 2–8 hours. Also known as Yperite or Yellow Cross.
Dichloromethyl chloroformate.	$Cl{\cdot}COO{\cdot}CHCl_2$	B.P. 116	L.I. Lach.	—	—	Not used by itself; present in trichloromethyl chloroformate.
Dichloromethyl ether	$(CH_2Cl)_2O$	B.p. 105	Lach.	Shell in admixture with ethyldichloroarsine and methyldibromoarsine.	Water.	N.I.
Dimethylsulphate	$(CH_3)_2SO_4$	B.p. 188	Lach. L.I.	Shell in admixture with methyl chlorosulphonate.	Alkalis.	N.I.
Diphenylamine arsenious chloride (phenarsazine chloride).	 $C_6H_4\langle{}^{AsCl}_{NH}\rangle C_6H_4$	M.p. 190–195 B.p. 410	L.I.	Generators.	—	Toxic smoke.

List of Chemicals which have been used in Warfare and their Characteristics—(*continued*).

1. Chemical name.	2. Formula.	3. Physical characteristics. °C.	4. Physiological action.	5. Method of use.	6. Neutralising agent.	7. Remarks.
Diphenylchloroarsine .	$(C_6H_5)_2AsCl$	M.p. 43 B.p. 333	L.I.	Shell by itself or mixed with phosgene and trichloromethylchloroformate ; can also be used in generators.	—	Toxic smoke.
Diphenylcyanoarsine .	$(C_6H_5)_2AsCN$	M.p. 35 B.p. 346	L.I.	Shell in admixture with ethylcarbazole. Can also be used in generators.	—	Very effective toxic smoke.
N-Ethylcarbazole . .		M.p. 68 B.p. 190	L.I. (slight)	Shell in admixture with diphenylcyanoarsine.	—	N.I.
Ethyldibromoarsine .	$C_2H_5AsBr_2$	B.p. 192–194	Leth. L.I.	Shell in admixture with dichloromethyl ether and ethyldichloroarsine.	Chloride of lime.	N.I.
Ethyldichloroarsine .	$C_2H_5AsCl_2$	B.p. 156	Leth. L.I.	Shell in admixture with dichloromethyl ether and ethyldibromoarsine.	Chloride of lime.	N.I.
Ethyl iodoacetate . .	$CH_2I{\cdot}COOC_2H_5$	B.p. 178–180	Lach.	Shell, T.M. bombs and grenades, often diluted with alcohol.	Caustic soda in glycerine.	Also known as S.K.
Hydrocyanic acid (Prussic acid).	HCN	M.p. −14 B.p. 26·5	Leth.	Shell and T.M. bombs in mixtures with chloroform and arsenic trichloride, with or without stannic chloride.	—	N.I.
Hydrogen sulphide .	H_2S	B.p. −61·8	Leth.	Cylinders with chloropicrin.	Alkalis or lime.	N.I.
Iodoacetone	$CH_3{\cdot}CO{\cdot}CH_2I$	B.p. 58 at 11 mm.	Lach.	T.M. bombs.	—	N.I.
Methyl chloroformate .	$ClCOOCH_3$	B.p. 71·4	L.I. Lach.	—	—	Not used by itself ; present in chloromethyl chloroformate.

Methyl chlorosulphonate	$SO_2Cl{\cdot}OCH_3$	B.p. 132	L.I.	T.M. bombs and shell mixed with dimethylsulphate.		N.I.
Methyldibromoarsine .	CH_3AsBr_2	B.p. 181	L.I.	Shell in admixture with ethyldichloroarsine and dichloromethyl ether.	Chloride of lime.	N.I. Used to a very slight extent.
Monochloromethyl chloroformate.	$ClCOOCH_2Cl$	B.p. 105	L.I. Lach.	Shell.	Sodium hypobromite and carbonate.	N.I.
Phenylcarbylamine chloride.	$C_6H_5{\cdot}NC{\cdot}Cl_2$	B.p. 209	Lach. L.I.	Shell.	—	N.I.
Phenyldichloroarsine .	$C_6H_5{\cdot}AsCl_2$	B.p. 252	L.I.	Shell.	—	N.I.
Phosgene (Carbonyl chloride).	$COCl_2$	B.p. 8·2	Leth. L.I.	Shell and T.M. bombs, by itself or mixed with chloropicrin; in shell mixed with stannic chloride or arsenic trichloride; in cylinders mixed with chlorine.	Alkalis; hexamethylenetetramine (hexamine) (in first gas mask).	Important war gas. Delayed effects.
Stannic chloride. . .	$SnCl_4$	M.p. −33 B.p. 114	L.I. (mild)	Grenades, by itself and in shell and T.M. bombs with chloropicrin, and in shell with phosgene and in hydrocyanic acid mixtures.	Water.	Largely used for smoke effect.
Sulphur trioxide (Sulphuric anhydride).	SO_3	M.p. 15 B.p. 46	L.I. (mild)	Grenades, T.M. bombs, and shell.	Alkalis.	Largely used for smoke effect.
Thiophosgene . . .	$CSCl_2$	B.p. 73	L.I. Leth. Lach.	Shell.	—	About as toxic as chloropicrin.
Trichloromethyl chloroformate (Diphosgene)	$ClCOOCCl_3$	B.p. 128	Leth. L.I.	Shell by itself or in admixture with chloropicrin or with phosgene and diphenylchloroarsine.	—	More persistent than phosgene.
Xylyl bromide . . .	$CH_3{\cdot}C_6H_4{\cdot}CH_2Br$ (mixture of ortho, meta, and para).	B.p. 216–220	Lach.	Shell, sometimes with bromoketone and benzyl bromide.	Alkalis.	N.I.

Chemical Products of Importance not used in Actual Warfare.

1. Chemical name.	2. Formula.	3. Physical characteristics °C.	4. Physiological action.	5. Method of use.	6. Neutralising agent.	7. Remarks.
Chloroacetophenone	$C_6H_5{\cdot}CO{\cdot}CH_2Cl$	M.p. 55·9 B.p. 245	Lach.	Could be used in generators or in solution in shell, T.M. bombs or cylinders.	Alkalis.	Powerful lachrymator, much used for anti-gas training.
Chloro-vinyl-dichloro-arsine (Lewisite).	$CHCl{:}CH{\cdot}AsCl_2$	M.p. −13 B.p. 190	V. Leth. L.I.	Could be used in shell or bombs.	Water and alkalis.	A very powerful war gas; product generally contains some ββ′-dichlorodivinyl-chloroarsine $(CHCl{:}CH)_2AsCl$ (b.p. 230), which is not quite so effective, and ββ′β″-trichlorotrivinylarsine $(CHCl{:}CH)_3As$ (b.p. 260°, m.p. 33°), which is still less active.
Methyldichloroarsine	CH_3AsCl_2	B.p. 132	V. L.I.	Could be used in shell and bombs.	Chloride of lime and alkalis.	—

37. Methyl chlorosulphonate : by the interaction of methyl alcohol ($CH_3{\cdot}OH$) and sulphuryl chloride (SO_2Cl_2).

38. Methyldibromoarsine : by the action of hydrobromic acid (HBr) on methylarsenious oxide (*see* Methyldichloroarsine).

39. Methyldichloroarsine : by the action of methyl sulphate[$(CH_3)_2SO_4$] on sodium arsenite (Na_2HAsO_3) giving disodium methylarsenite [$Na_2(CH_3)AsO_3$] which on reduction by sulphur dioxide (SO_2) to methyl arsenious oxide ($CH_3As{\cdot}O$) and subsequent treatment with hydrogen chloride gives the desired product.

40. Monochloromethyl chloroformate : by the interaction of methyl alcohol (CH_3OH) and formic acid ($HCOOH$), and the regulated chlorination of the resultant methyl formate ($H{\cdot}COOCH_3$).

41. Phenylcarbylaminechloride : by the direct action of chlorine on phenyl carbylamine ($C_6H_5{\cdot}NC$), or on phenyl *iso*thiocyanate ($C_6H_5{\cdot}NCS$).

42. Phenyldichloroarsine : *see* diphenylchloroarsine.

43. Phosgene : by the combination of chlorine and carbon monoxide (CO) in the presence of a catalyst, usually charcoal ; either diluted carbon monoxide, such as in producer gas, or concentrated carbon monoxide may be used.

44. Stannic chloride : by the action of chlorine on tin.

45. Sulphur trioxide : by the catalytic oxidation of sulphur dioxide (SO_2) derived from burning sulphur or pyrites.

46. Thiophosgene : by the regulated chlorination of carbon disulphide (CS_2).

47. Trichloromethyl chloroformate : by complete chlorination of methyl formate

$$(H{\cdot}COOCH_3)$$

or of chloromethyl chloroformate (*q.v.*).

48. Xylyl bromide : by the bromination of boiling xylene [$C_6H_4(CH_3)_2$].

Literature References. — The literature on chemical warfare is now so large (running into well over 1,000 different publications) that it is only possible to give a limited number of references to the more important textbooks. These are appended under the following four headings :

A. Textbooks (covering historical, defensive, and offensive aspects).
B. Defensive.
C. Medical.
D. Offensive.

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CHEMICAL WARFARE DEFENCE.

Gas Defence.

Historical and General.—The basis of defence against gas is the respirator, or gas mask. When the employment of gas in warfare was initiated by the use of chlorine in 1915, protection for British troops was obtained by the use of pads of flannel, cotton wool, or cotton waste placed over the mouth and nose and soaked in a solution of sodium thiosulphate (hypo) or of this compound with sodium carbonate. Subsequently the gas mask took the form of a helmet soaked in a solution of hypo, sodium carbonate, and glycerin, covering the whole of the head and fitted with mica windows. With the threatened use of phosgene, an impregnating solution of sodium phenate was used for the gas helmet (P. helmet), and was subsequently improved by the addition of hexamethylenetetramine (hexamine) (P.H. helmet), which also gave protection against hydrocyanic (prussic) acid. The use of tear gas introduced the need for wearing goggles in addition to the helmet, but the combination was not very satisfactory. As gas warfare developed, the employment of chemical neutralising agents for protection against the variety of gases used and the increasing concentrations became impracticable with a respirator of the helmet type, and a gas mask, called the box respirator, was produced by the British to deal with all types of gases. This consisted of an air-tight mask or covering for the face fitted with eye-pieces of mica, celluloid, or splinterless glass; to this mask was attached by a connecting tube the box or container in which were placed the materials for the purification of the air breathed by the wearer. This type of construction with a face-piece connected directly or by a tube to a container constitutes the basic principle on which practically all gas masks for war purposes have since been designed. The main exception was the French M.2 mask, which covered the whole face (eye-pieces being provided) and consisted of a number of layers of muslin impregnated with various absorbent chemicals. One mixture contained hexamine, nickel sulphate, sodium carbonate, glycerin, and water, and another castor oil, alcohol, sodium hydroxide, glycerin, and water. Such masks are very inferior to the face-piece and container type.

Modern gas masks are practically all based on the principle of a face-piece connected to a container of neutralising, absorbing, or filtering materials. The differences in the various designs are essentially differences in details introduced with a view to securing greater service efficiency in one direction or another.

Respirator Face-pieces.—Face-pieces may be of many kinds. There are full masks covering the eyes, nose and mouth, and half-masks which do not cover the eyes. The latter are useless where gases which irritate or injure the eyes are present; therefore the full mask is always preferable, because, furthermore, it is likely to be more gas-tight and comfortable. There are also hoods covering the whole head. The main parts of a face-piece are:

(1) *The body,* generally of rubber, with or without a covering of stockinette or other elastic textile material on the outside. It can also be made of leather, of rubberised fabric in single or multiple layers, of canvas with or without edgings of rubber, leather, etc., to give a gastight joint, or of asbestos. There are also designs in transparent celluloid or cellophane, so that the wearer's face can be seen.

(2) *Eye-pieces,* generally round, but sometimes oval and fitted with discs of celluloid or of splinterless, laminated, or plain glass, to the inside of which may be attached gelatine discs to absorb moisture and to prevent fogging due to the moisture in the expired air. The fogging may be obviated by using what is called the Tissot principle, by which the inhaled air passes over the eye-pieces and prevents condensation of moisture. Alternatively or in addition, anti-dimming paste may be applied to the glass. A typical anti-dimming paste can be made from Turkey red oil and water glass. For military use, it is important that there should be an adequate field of vision and that it should be possible to use optical instruments such as binoculars and range-finders.

(3) *Head harness* for adjustment to the head, usually consisting of elastic or spiral metal springs covered with fabric. The bands are generally adjustable to suit the wearer's face. A well-fitting and gas-tight mask should not feel uncomfortable on the face if the design is good.

(4) *A valve holder,* for an outlet valve or alternatively an attachment in metal for the container or the connecting tube. The outlet valve, where there is one, is generally of rubber. Designs in metal are known, but these are generally for inlet valves, which may be in the face-piece, connecting tube, or container. The outlet valve is one of the vital parts of a respirator as a leakage might be fatal to the

wearer. Great ingenuity has been displayed in designing types which are leak-proof under all conditions, and at the same time give good speech transmission. In respirators with directly attached containers there is often no outlet or inlet valve, and the wearer breathes in and out through the filtering box. Certain advantages are claimed for this in the way of increased protection, but it is generally more oppressive to wear.

Face-pieces are generally made in three sizes to fit all kinds of face, but a well-designed mask of normal size should, by proper adjustment, give complete protection to well over 90% of adult male faces. Types of face-pieces with nose clip and mouthpiece, which were largely used in the war but were very uncomfortable, are now practically obsolete.

The design of a respirator face-piece has to be a compromise between a number of conflicting requirements. It must be gas-tight and comfortable to wear. It must not unduly interfere with vision or with speech, whether direct or through telephones or voice pipes, and it must not impede the wearer in the course of his duties. With the best designs of gas mask the loss of service efficiency is less than 20%.

Respirator Containers.—The main chemical interest is in the container, sometimes called the box, drum, or canister, which holds the filtering materials. Containers are generally rectangular or round, and in the normal design, the air enters at the bottom and passes through the filtering and absorbing material, which is generally arranged in horizontal layers. In a few designs, the air enters at the sides, passing through the filtering materials to a central tube connecting with the face-piece. It is not necessary to give details of the internal mechanical structure of a container which can be seen from diagrams, except to say that it is no easy matter to arrange the filtering materials so that they will be effective and remain so under the various conditions of rough handling they may receive in use.

The basic constituent in most respirator containers is active carbon or charcoal, the efficiency of which as an all-round adsorbent for gases and vapours has steadily improved since its first utilisation for gas defence in 1915. The charcoal is used in the form of granules containing generally from 15 to 25% of moisture. This moisture enhances the value of the charcoal for the catalytic decomposition of gases such as phosgene, but reduces its adsorptive capacity for organic vapours. So great is the all-round efficiency of active carbon that some military respirators rely on it entirely for gas protection. It is not, however, active against carbon monoxide, which for physical and physiological reasons is not likely to be used as a chemical warfare agent, nor is it very effective against oxidisable gases such as arsine (arseniuretted hydrogen) or prussic acid. A special mixture of copper and manganese oxides known as *hopcalite* can, however, be used for the catalytic oxidation of carbon monoxide, if required, but this necessitates the provision of an extra layer of drying material such as calcium chloride in front of the hopcalite which soon loses its activity in moist air. The protection against arsine and prussic acid can be improved by the use of granules generally of an alkaline nature and consisting, for example, of soda lime in combination with permanganate. Such granules were used in the British respirator, and not only gave good protection against these two gases, but also against acid gases generally. The value of active carbon as a generally protective agent against poisonous gases can always be enhanced by other types of chemical granules designed to improve the neutralising properties of the container against any particular chemical warfare agent employed. The effectiveness of charcoal as a protection against phosgene can be greatly increased by impregnating it with hexamine. Such chemical granules are to be found in the containers of respirators designed to deal with special toxic gas hazards in industry (*see below*). The granule is in effect an active chemical neutralising agent for the particular gas which has to be encountered. Granules may be of two distinct types. The actual chemical or mixture of chemicals may be compressed and then broken up into suitably sized pieces, or fragments of a porous material, such as pumice, kieselguhr, or brick, may be soaked in the chemical and dried.

Neither active carbon nor chemical granules afford protection against fine particles such as are present in screening and toxic smokes, and all service respirators incorporate a filtering material of some sort for dealing with such smokes. These filters vary considerably in composition and efficiency. The principal substances used for making filters are cotton wool, merino wool, animal hair, wood and other paper pulps, cellulose sheets or wadding, feathers, and felt. Their filtering efficiency may be increased by depositing upon them fine smoke particles such as the smoke from burning camphor, naphthalene, or resins or by mixing them with fibrous materials such as asbestos or with finely powdered lampblack, or cuprene (a solid condensation compound of acetylene) or by depositing nodules of certain gums and resins on them from solution. The difficulty of obtaining a compact efficient filter with a low resistance to breathing has been overcome by various ingenious methods of folding and arranging the layers of filtering material, so that a large filtering area can be compressed into a small space. The best filters now available give a very high standard of protection against even the most penetrative toxic smokes and will remove more than 99% of the toxic material from the air breathed.

Industrial Respirators.—Industrial gas masks differ fundamentally from service gas masks in their essential desiderata. The service gas mask has to protect against any concentration that may be encountered of any toxic substance capable of use as an agent of chemical offence. It has, therefore, to be polyvalent. Fortunately, many toxic substances such as carbon monoxide and arsine, against which it is difficult to protect by a filtering apparatus, cannot, for technical reasons, be employed in the field. Further, there is a limit to the concentrations that may be met. A concentration of 1% is exceptional, while from artillery shell, with which most of the gas attacks were delivered in the latter part of the war, a concentration as high as 1 in 1,000 is unusual. For toxic smokes, 1 in 1,000,000 is a high concentration. Thus, the problem is one of protection against comparatively low concentrations of many different gases.

In industry, the real function of the respirator is as an emergency device to deal with unusual circumstances such as the closing down of a leaking valve emitting toxic vapour or the rescue of a man from a dangerous area. Therefore, in industry, when a respirator has to be used, it may be in a confined space and the concentration may be very high indeed, even as much as a few per cent. of the toxic vapour. On the other hand, in any particular works or plant, the danger is generally limited to one or two gases at most. It is therefore possible to design the respirator specially for the gases to be encountered, and so provide a much higher protection against them than is possible in a polyvalent respirator. This means that for industry a number of different types are required to cope with all its gas hazards.

The service respirator may have to be worn in action for long periods of time ; consequently it must be very comfortable to wear and provide good vision and good facilities for ordinary and telephonic speech. An emergency device, as in industry, does not need the same standard of comfort for short-period wear, or even of vision or speech, though obviously these should all be good. On the other hand, the gas tightness of the industrial respirator must, if anything, be superior to that of the service type because of the higher concentrations. The service respirator therefore is a different problem from the industrial, and is not necessarily suitable for meeting the hazards of industry.

The face-piece of the industrial gas mask calls for no special comment, as it is very similar to that used for service purposes. The main difference is in the container. Different types of container are generally produced to deal with different industrial gases or types of gases or for combinations of types. The following is an indication of the types of neutralising or absorbing materials used for various purposes in industrial gas masks.

(1) *Organic vapours,* such as benzole, acetone, carbon tetrachloride, carbon disulphide, formaldehyde, and toluene. The usual adsorbent is active carbon or charcoal. Against most organic vapours it is excellent, but it is poor against methyl bromide and methyl chloride ; provided it is not too dry, it functions fairly well against acid gases such as phosgene. It is asserted by one authority that active carbon will stop effectively all gases and vapours with a molecular weight greater than 50. Silica gel can in some cases replace active carbon, but its best value is against water soluble gases.

(2) *Acid gases,* such as hydrocyanic acid, nitric acid, formic acid, free halogens, nitrous fumes, phosgene, and sulphur dioxide. Among the adsorbents used are (*a*) soda lime or other alkaline granules, (*b*) diatomite, brick, pumice or similar material impregnated with caustic soda, potassium carbonate, sodium bicarbonate and/or zinc acetate. Active carbon may be used in addition to these adsorbents.

Other adsorbents used are based on potassium metasilicate ; hexamine, which is a good adsorbent for phosgene ; zincates and zincammines. Soda lime granules impregnated with permanganate will give enhanced protection against hydrocyanic acid, as will also *hopcalite*, the carbon monoxide neutraliser referred to later. Sometimes a special container is designed to deal with hydrocyanic acid and other weak acids. Diatomite impregnated with finely-divided mercury oxide or certain complex zinc salts is used for this purpose.

(3) *Ammonia,* the main adsorbents being (*a*) salts of copper, such as copper sulphate impregnated on pumice (often known as *kupramite*), (*b*) salts of zinc and cobalt, (*c*) salts of copper and nickel, and (*d*) silica gel.

(4) *Hydrocyanic acid and carbon dioxide.*—A good adsorbent is baryta granules.

(5) *Sulphuretted hydrogen.*—A good adsorbent is a mixture of baryta granules and active carbon.

(6) *Nitrous fumes.*—Alkaline permanganate granules and hopcalite are very useful.

(7) *Sulphuretted hydrogen and ammonia.*—Adsorbents used are (*a*) copper chloride on a solid support which can be active carbon or activated mineral salt, (*b*) silica gel, (*c*) mixture of baryta granules, charcoal and copper sulphate granules.

(8) *Carbon disulphide,* for which lead and manganese peroxides can be used.

(9) *Carbon monoxide,* against which the gas mask of the fighting services affords no protection. This gas is present in producer gas, blast-furnace gas, coal gas, water gas, after-damp in mines, etc. As carbon monoxide in any quantity is very often associated with a lack of oxygen, reliance is generally placed on a self-contained oxygen apparatus when men have to go into such an atmosphere. Of recent years, however, much attention has been devoted to the development of a filter mask for carbon monoxide. This has involved the production of a material for the catalytic oxidation of carbon monoxide at ordinary temperature. The product in most general use is called *hopcalite,* which is a mixture of manganese dioxide and copper oxide. Hopcalite will function only in dry air, so the incoming air has to be dried, for example, by a layer of calcium chloride or silica gel. Behind the hopcalite there has to be a layer of alkaline material, such as soda lime granules, to remove the carbon dioxide formed in the oxidation of the monoxide. The hopcalite will act indefinitely, so the life of the container depends on the capacity of the drier. Much heat is generated in the oxidation and the container will get very hot if there is much over 1% of monoxide in the inspired air, while the air will get too hot to breathe unless cooling layers, for example, of sodium thiosulphate pentahydrate, are interposed. It is stated that 1% of carbon monoxide will on oxidation give off enough heat to raise the temperature of the air adiabatically

about 100°C. The oxidation uses up oxygen equal to half the volume of the carbon monoxide so that where there is much carbon monoxide the oxygen content in the purified air is likely to be low.

Hopcalite has remarkable properties as an oxidising agent, and will also deal efficiently with ammonia, hydrogen cyanide, hydrogen sulphide, arsine, nitrous fumes, phosphine, and ethylene. Its main defect is its sensitiveness to moisture, which at present is its limiting feature.

Another adsorbent for carbon monoxide, known as *hoolamite,* is based on the oxidising properties of iodine pentoxide and concentrated sulphuric acid. The mixture is generally used impregnated on pumice with a subsequent layer of active carbon or alkali granules to absorb the iodine liberated in the oxidation.

As carbon monoxide is tasteless and odourless and produces no immediate symptoms to reveal its presence, the question of a detector to indicate when a container is becoming exhausted is of first-class importance. With most other gases there is ample warning because of the odour, taste, or irritating effect produced from the first traces of gas that penetrate the respirator ; nevertheless, in some designs visible detectors depending on a colour change are fitted. The problem of detecting carbon monoxide has been attacked from many angles, and the following methods for indicating when a container should be changed have been used :

(*a*) Mechanical timer. This is operated by the breathing and depends merely on the number of inspirations the wearer has made through the container, whether there is any carbon monoxide there or not. It will, as a rule, show the container to be exhausted long before it is so.

(*b*) Hoolamite detector.—In this detector, when the carbon monoxide passes through the oxidising layer of hopcalite and impinges on the hoolamite, it liberates iodine which gives a warning by its irritating action on the nose and throat that the container is almost exhausted. Alternatively, it has been suggested that the iodine can be made to liberate chlorine which, combining with carbon monoxide, will give phosgene which is readily detectable by the wearer.

(*c*) Calcium carbide.—When water vapour penetrates the hopcalite layer—which it will do when the drier is saturated—it will in contact with the carbide liberate acetylene, which gives a warning odour.

(*d*) Colour change.—This is obtained by the effect of humidity on various salts, such as dehydrated cobalt chloride, copper sulphate or platinocyanides. These are placed between the drying material and the hopcalite and will change colour when the drier is letting water vapour pass, thus indicating that the hopcalite will soon cease to act. Colour changes are not very reliable and are not easy to observe in dimly-lighted places.

Carbon monoxide respirators have not been used to a great extent in this country as there is always the danger, especially in mines after an explosion, that the rescuers may lose their lives in the event of their encountering a region with an inadequate percentage of oxygen in the air. They could, of course, get ample warning of an oxygen deficiency by the use of a test lamp. In many cases no danger from oxygen shortage will exist, and then the carbon monoxide gas mask can be used to advantage, as it will impose less strain on the wearer if he has to do work than will the heavier self-contained apparatus. Apart from mines, there are other cases, for example, near blast-furnaces, where a shortage of oxygen will be accompanied by a high concentration of carbon monoxide, but the latter will immediately make itself noticeable by the rapid heating of the container and thus give a warning.

To stop industrial smokes, dusts and fumes, the filtering materials used in service respirators can be employed.

Designs have been produced for all-purpose respirators intended for use primarily by firemen who may have to encounter in fire fighting a large variety of gases including carbon monoxide and smoke. Such a container is made up from a combination of the adsorbents required to protect against the various hazards, and a typical container of this sort on the market consists of the following layers from the bottom to the top ; (*a*) active carbon for organic vapours ; (*b*) cotton wool for smokes, fogs, and dust ; (*c*) caustic soda impregnated on pumice for acid gas ; (*d*) cotton wool for smokes ; (*e*) fused calcium chloride as a drying layer ; (*f*) hopcalite to oxidise carbon monoxide ; (*g*) silica gel or carbon impregnated with copper sulphate to stop ammonia. Various other combinations are of course possible. A general adsorbent for gases other than carbon monoxide could be based on sodium carbonate, zinc acetate, magnesium peroxide, and powdered charcoal.

Protection for Animals.—Respirators have also to be provided for animals such as horses, dogs and pigeons in their baskets. These generally take the form of a bag or covering of thick material impregnated with a chemical solution such as was used in the early gas helmets, but they are not very satisfactory in practice.

Collective Protection.—The problem of providing protection for closed rooms and compartments in which people can work without gas masks is solved by the use of purification units constructed on the same general principle as the container of the respirator, through which air is drawn into the room or compartment by means of a fan, preferably from an area likely to be free from gas such as the top of a high building or a chimney stack. The methods of air regeneration used, for example, in submarines can also be employed, but are in general less convenient and more expensive. For the protection of dug-outs and rooms in the fighting area, curtains of thick cloth impregnated with a chemical solution or a heavy mineral or a vegetable oil such as cylinder or linseed oils, are used at the entrances, two curtains with an air lock between being generally provided for greater security.

Protection against Mustard Gas.—The introduction of mustard gas with its action on the skin presented a new problem in protection which has not yet been properly solved. Garments of oilskin and other impervious materials, if of air-tight design, give a fair measure of protection, but can only be worn for comparatively short periods in view of the stifling effect on the wearer, especially in hot weather. The use of clothing impregnated with a chlorinating agent such as chloramine or allied products which will destroy mustard gas has also considerable limitations, while protective ointments of vaseline or of zinc oxide and fat mixtures, with or without a chemical to neutralise the mustard gas, are also of doubtful utility under service conditions, though they may be of some value in certain circumstances.

Decontamination.—Another problem in gas defence is the decontamination or clearing of areas which have been contaminated with a persistent gas, especially if it is of the mustard gas type, against which a gas mask is not a complete protection because of its general action on the skin. Generally speaking, water, and earth are the only materials available in adequate quantity if extensive decontamination has to be done, and they can be used to wash away the mustard gas liquid or cover up the infected area. Where available, bleaching powder diluted with about 3 times its volume of an inert material such as sand or earth is the most effective substance to use. The neutralising agents mentioned in column 6 of the table on pp. 12–15 on chemical warfare agents can also be used for dealing with the gases against which they are effective. For the decontamination of textiles and general clothing a number of methods can be used depending on the type of garment and the extent of the contamination, such as exposure to the weather, washing, solvent extraction, or treatment with steam or hot air.

Detection of Gas.—Another problem of chemical interest is the use of detectors to indicate the presence of gas. While detecting papers, paints or solutions can be provided to deal with substances such as chlorine and mustard gas, the devices as a rule are not sufficiently simple, quick, or certain in their action to make their adoption desirable except under special conditions and in the hands of trained observers. Reliance has in practice to be placed on the sense of smell and the sensory organs generally.

Protection of the Civil Population against Gas.—One of the most important problems of the present day is the protection of the civil population at large against gas attacks from the air. These attacks may be made with bombs containing gas, or by spraying liquids of high boiling-point, like mustard gas, from aircraft. Those members of the community who must continue to carry on their duties either during or immediately after a raid and the members of the defensive organisations must be provided with gas masks, in the same way as service personnel, and with a certain amount of protective clothing depending on the nature of the work they have to do. Those of them, like the police and the fire brigades, who will have to perform their duties whatever the conditions, will be equipped with service respirators. For the others, a somewhat simpler and cheaper respirator called the civilian duty respirator will suffice. For the civilian population at large the main defence will be gas protected rooms in their own houses or offices, the rooms being selected with due regard to the fact that high explosive and incendiary bombs are certain to be used as well as gas. Public shelters, ventilated with air purified by passage through filtration units, will be required for people caught in the streets, and similar shelters may be installed by important organisations. The public will have to seek the shelter of their gas protected rooms immediately the air raid warning is given. As a second line of defence to be used if the gas protection of the room is damaged or if a contaminated area has to be evacuated, the public will be provided with a simple but effective design of gas mask called the general civilian respirator.

In addition, arrangements will have to be made for :

(*a*) a gas detection service to examine the bombed areas, diagnose the nature of the gas used (if any), and indicate whether decontamination is required or not,
(*b*) decontamination squads to render the bombed areas safe to occupy,
(*c*) a first aid service to deal with casualties, which must include first aid and decontamination centres for the treatment of the less serious casualties and the decontamination of the persons and clothing of people who may be contaminated with gas, and
(*d*) casualty clearing stations and hospitals for the more severe cases.

These services will form part of the general air raid precaution services required to deal with all types of air raid and the detailed organisation will be the responsibility of the local authorities. The necessary technical details will be found in the series of Air Raid Precautions Handbooks which are issued periodically by the Air Raid Precautions Department of the Home Office and are obtainable from H.M. Stationery Office.

J. D. P.

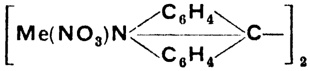
CHEMICKING *v.* BLEACHING.

CHEMILUMINESCENCE. — Accepting the term " luminescence " to denote emission of light other than that due to temperature effects, " chemiluminescence " should denote the direct conversion of the free energy of chemical reaction into light energy. As, however, mere change in the energy levels of atoms may result in change of chemical properties and thus be considered as chemical action, and as possibly all radiation of wave-length shorter than the infra-red is due to release of this store of intra-atomic energy, a logical application of modern views would include all forms of luminescence as chemiluminescent phenomena. The usual but undefined terminology therefore restricts the term to those instances when light appears as a result of the formation of molecules of high energy levels during the production of *new substances.* In this sense the inclusion of, for example, such phenomena as crystallo- and tribo-luminescence is questionable; light emitted during crystallisation of, say, sodium chloride may be ascribed to recombination of ions and as it seems significant that the colour is the same for both emissions when they can be observed in a single salt (Weiser, J. Physical Chem. 1918, **22**, 439) a similar explanation should hold for triboluminescence, and its inclusion among chemiluminescent phenomena in the above modified sense should then depend on the demonstration of chemical differences between crystals capable of exhibiting triboluminescence and aged crystals no longer possessing such ability. Again, in addition to the traditional use of the term "phosphorescence," this term is also used to denote the delayed emission of light by a substance after previous illumination, fluorescence being the instantaneous reversal of illumination, and it is difficult to decide whether such phenomena are dependent on chemical action in the above sense. Thus Chakravarti and Dhar (Z. anorg. Chem. 1925, **142**, 299) were unable to confirm the suspected relationship between fluorescence and oxidation of certain organic dyes, but a chemiluminescent interpretation is not easily disproved in other cases. The luminescence of slightly impure zinc sulphide on bombardment with α-particles is another border-line instance.

The liberation of part of the energy of interaction between molecules or atoms in the restricted sense may be the result of one of two mechanisms (Wegscheider, Rec. trav. chim. 1923, **42**, 585): (*a*) the energised atoms or molecules emit radiation directly, or (*b*) the excess energy may be transferred to other molecules which can then emit their own characteristic radiation. Although these conceptions have been experimentally realised in some instances, the mechanism of the majority of known instances of chemiluminescence is quite undetermined, our knowledge being limited to the visual observation of light. The following examples are therefore arbitrarily classified according to the physical state of the luminescing system.

The luminescent oxidation of phosphorus vapour is among the best known of the phenomena under review (Chariton and Walta, Z. Physik, 1926, **39**, 54), although still not completely understood (Downey, J.C.S. 1924, **125**, 347; Emeléus and Purcell, *ibid.* 1928, 628). F. Schacherl (Gazzetta, 1932, **62**, 610) finds that phosphorus oxychloride exerts a positive catalytic effect and postulates the formation of the oxide P_4O to explain the emission of light. Aerial oxidation of many organic vapours, *e.g.* ether, carbon disulphide, etc., produces "cold" luminous flames, while the light of the "non-luminous" Bunsen flame is a true instance of chemiluminescence. Oxidation of a 2% mixture of heptane in air producing visible radiation (H. Beatty and G. Edgar, J. Amer. Chem. Soc. 1934, **56**, 102), the reaction between hydrogen and chloroform (H. Fromherz and H. Schneller, Z. physikal. Chem. 1933, **20**, 158), polymerisation of acetaldehyde in presence of active hydrogen (H. Urey and G. Lavin, J. Amer. Chem. Soc. 1929, **51**, 3286), reaction of sodium vapour with chlorine (Lialikow and Terenin, Naturwiss. 1926, **13**, 83; Z. Physik, 1926, **40**, 107), the "afterglow" of active nitrogen (Bonhoeffer, Z. Elektrochem. 1926, **32**, 536), etc., are all further instances of luminescent reactions in the gaseous phase.

Some inorganic reactions in solution are known to be chemiluminescent, *e.g.* many oxidations, the catalytic decomposition of hydrogen peroxide by silver, platinum, etc., and the neutralisation of some oxides by conc. sulphuric acid. The great majority of known cases, however, are furnished by the oxidation of organic materials. Many aldehydes (Radziszewski, Ber. 1877, **10**, 321; 1883, **16**, 597), sulphur compounds (Delépine, Compt. rend. 1912, **154**, 1171), Grignard compounds (Lifschitz, Helv. Chim. Acta, 1918, **1**, 472; Dufford, Calvert and Nightingale, J. Amer. Chem. Soc. 1923, **45**, 2058; 1925, **47**, 95; Evans and Diepenhorst, *ibid.* 1926, **48**, 715) are luminescent on direct oxidation or on reaction with picryl chloride (Wedekind's reaction), that of phenanthryl-9-magnesium bromide being particularly intense (W. Bachmann, J. Amer. Chem. Soc. 1934, **56**, 1363). Many dyes and phenolic compounds exhibit the phenomenon when oxidised with hydrogen peroxide or ozone in presence of ferrous sulphate (N. Biswas and N. Dhar, Z. anorg. Chem. 1928, **173**, 125; 1930, **186**, 154; 1931, **199**, 400). The emission of light on oxidising organic hydrazides is not uncommon, *e.g.* benzhydrazide, benzene sulphonhydrazide, and substituted derivatives (A. Witte, Rec. trav. chim. 1935, **54**, 471) that emitted by 3-aminophthalhydrazide being spectacular as it is visible in a dilution of $1:10^8$ an intensity exceeded only by the luminescence accompanying the oxidation of NN′-dimethyldiacridylium nitrate (I)



I.

which is visible in a dilution of $1:10^{10}$ (K. Gleu and W. Petsch, Angew. Chem. 1935, **48**, 57) (*v.* Acridine, Vol. I. p. 130*r*).

Crystallo- and tribo-luminescence have already been quoted as extreme examples of chemiluminescence among solids. Others are the reaction between antimony and chlorine (S. Bhatnagar and K. G. Mathur, Z. physikal. Chem. 1930, **9B**, 229), and the oxidation of solid sodium which is non-luminous in pure dry oxygen but becomes luminescent in presence of a trace of water vapour, H_2S, dry HNO_3 vapour, or dry AcOH vapour, but not SO_2 or the halogens (R. Bowie, J. Physikal Chem. 1931, **35**, 2964).

Interpretation of certain bright lines in stellar spectra as due to chemiluminescence has been proposed (K. Wurm, Z. Astrophys. 1935, **10**, 133) while, on the other hand, the luminescent bacterial and fungal phenomena of dead fish, meat, wood, etc., have given rise to much work (bibliography, E. Harvey, Bull. Nat. Res. Council, U.S.A. 1927, **59**, 50). Emission of light is not dependent on the living cell and is, indeed, in some species an extra-cellular phenomenon, being, in fact, due to the interaction of two materials, *luciferin* and *luciferase*, in presence of oxygen. These may be separately purified and are remarkably specific, no light being emitted unless both components are obtained from the same or very closely related species ; although considerable knowledge of the conditions governing the luminescence has been collected, the ultimate structural nature of these components is unknown. Luciferin has many of the properties of a peptone, and functions with its oxidation product oxyluciferin as a reversible system. The oxidation of luciferin is effected by many oxidising agents but never with luminescence. Luciferase possesses the properties of an albumin and appears to behave somewhat as an enzyme in the liberation of light.

It is unfortunate that the intensity of chemiluminescence is in general so small that the quantitative aspect has been somewhat neglected. Intensity of emission has sometimes been conveniently determined by visual methods of substitution such as were used by C. Thomas and R. Dufford (J. Opt. Soc. Amer. 1933, **23**, 251) when studying the chemiluminescence of Grignard compounds, but the sensitised photographic plate or moving film presents advantages, *e.g.* for recording rapid fluctuations in intensity (Amberson, J. Gen. Physiol. 1922, **4**, 517). Methods employing a photoelectric cell enabling very feeble sources to be studied are particularly valuable ; A. Pospelow, B. Pyatnitzki, and S. Zhurkow (J. Russ. Phys. Chem. Soc. 1929, 631 Phys. Pt.) have studied in this way the luminescence of amarine and lophine when oxidised with bromine water. The spectral distribution of the emitted light is determined by spectroscopic means, although when the source is too feeble the use of a series of colour screens of graded limits of transmission yields fairly accurate quantitative results (*see* Weiser, J. Physical Chem. 1918, **22**, 439).

Quantitative study of chemiluminescent phenomena has been concerned chiefly with (*a*) spectral observations, (*b*) energetics and efficiency (Bull. Nat. Res. Council, U.S.A., 1927, **59**, 1). Outstanding conclusions are the recognition of a general band and not a line spectral character; the fact, deducible on theoretical grounds (Harvey, J. Gen. Physiol. 1925, **8**, 89), that for the emission of light there must occur a state richer by 37–71 cals./mol. than another condition to which transition occurs spontaneously. This energy limitation is certainly not the only condition that luminescence shall occur and may in a complex reaction only apply to an individual stage in the process so that it is not inevitably required that the total energy of reaction should lie within these limits. Thus the chemiluminescent decomposition of the iodide of Millon's base is actually endothermic (Z. Petrikaln, Z. Physik, 1925, **32**, 569). It would then seem that estimations of the efficiency of chemiluminescent processes (*i.e.* the percentage of the total heat energy emitted as light) can only be of direct significance when the reaction is simple, and is rather of comparative value in the study, for instance, of a series of related compounds. Even here relationships are so obscure that generalisations are rarely possible, *e.g.* Lifschitz and Kalberer (Z. physikal. Chem. 1922, **102**, 393) studying the oxidation of Grignard compounds could trace no connection between the appearance or non-appearance of luminescence and heat of reaction. Nevertheless, estimations of efficiency have revealed at least the one remarkable fact that while the efficiency of " pure " chemiluminescent reactions is in general very small ($<1\%$), that of bioluminescent processes seems uniformly high. Thus, while the light efficiency of the (incomplete) combustion of phosphorus vapour in air was calculated to be ·00011% (Adams, Physical Rev. 1924, **23**, 771), Karrer estimates the luminescence efficiency of the firefly to be as high as 19·4% (J. Franklin Inst. 1918, **185**, 775).

Among a number of reviews of general and special aspects of chemiluminescence may be mentioned the following: F. Schacherl (Atti congresso naz. chim. pura appl., 1933, **4**, 599; E. Rideal, Chem. News, 1929, **139**, 36; Bull. Nat. Res. Council, U.S.A., 1927, **59**, 1; H. Beutler, Angew. Chem. 1932, **45**, 249 (theoretical); J. H. Graham, Amer. J. Pharm. 1935, **107**, 245 (chemiluminescence and biophotogenesis).

CHEMISORPTION *v.* CATALYSIS IN INDUSTRIAL CHEMISTRY. Vol. II., p. 422*r*.

CHENODEOXYCHOLIC ACID *v.* BILE.

CHENOPODIUM, ESSENTIAL OIL OF. American wormseed oil. The oil distilled from the flowering and fruiting plants of *Chenopodium ambrosioides*, var. *anthelminticum* A. Gray (Chenopodiaceæ), a native of Central America and the West Indies. The commercial oil is distilled chiefly in Maryland and is known as Baltimore oil. Great care is required during distillation as the chief constituent is decomposed by overheating. High pressure steam is used and the distillation carried out as rapidly as possible. Yield 0·6 to 1·0%.

Constituents.—The main constituent is ascaridole (*q.v.*) a body closely related to cineole, having a peroxide structure. Ascaridole decomposes with explosive violence on heating to 130°–150°. Other constituents are *p*-cymene, terpinene, $\Delta^{2\text{-}8(9)}$menthadiene, and traces of butyric acid, safrole, and methyl salicylate.

Characters.—A colourless or pale yellow liquid with a disagreeable, penetrating camphoraceous odour and a burning, bitter taste. Sp.gr. 0·960–0·980 at 15·5°, optical rotation −4° to −8°, n_D^{20} 1·474-1·479. Soluble in 3 to 10 vols. 70% alcohol. Contains not less than 65% ascaridole, determined by the process described in the " British Pharmacopœia." It is employed in medicine as an anthelmintic for the treatment of hookworm and round-worm.

C. T. B.

CHERIMOYA. The fruit of *Anona Cherimolia* Mill. It is apparently indigenous to certain districts of Ecuador, and is cultivated in Mexico and other tropical regions of South America. The fruit somewhat resembles the pineapple in shape and may be either smooth or spiny, weighing 0·5–1 lb. Its characteristic flavour results from its high sugar content modified by the presence of various acids.

Thompson (Hawaii Agric. Exp. Sta. Rept. 1914, 62) recorded the following analysis of the fruit: total pulp 84%, total solids 33·8%, protein 1·84%, fat 0·15%, acids (as malic) 0·09%, reducing sugars 15·34%, sucrose 3·07%, fibre 4·29%, ash 0·67%.

A. G. Po.

CHERRY. The fruit of *Prunus avium* L. (or *P. Cerasus*, var. *avium*), the sweet cherry, and of *P. Cerasus* L. (or *Cerasus vulgaris* Mill.), the sour cherry. The latter are also known as Morello cherries (dark varieties) or amarelles (light varieties). Cherries are utilised as dessert and culinary fruit or may be canned, dried or candied. Maraschino cherries used in confectionery are sweet cherries bleached with sulphur dioxide, split and stoned, dyed with Ponceau 3R, and preserved in syrup. The liqueur maraschino is prepared from the sour cherry. Black Forest and Swiss "Kirschwasser" is distilled from fermented sweet cherries.

The composition of the flesh of cherries, which represents 94–95% of the weight of the whole fruit, averages (% fresh weight):

	Total solids.	Protein.	Acid (as malic).	Invert sugar.	Sucrose.	Ash.
European[1]	14·5	1·26	0·51	12·0	0·5	0·4
European[2]	14·2	—	0·73	9·6	—	0·6
American[3]	18·7	0·91	0·43	10·4		0·5

[1] Kulisch, Z. angew. Chem. 1894, **7**, 148.
[2] Olig, Z. Unters. Nahr.-Genussm. 1910, **19**, 558.
[3] Shaw, Oregon Agric. Exp. Sta. Bull. 1898, No. 55.

Windisch and Schmidt (Z. Unters. Nahr.-Genussm. 1909, **17**, 584) record the following analyses of the juice of sour and sweet varieties as:

	Sp.gr. 15°.	Total solids.	Protein.	Acid (as malic).	Invert sugar.	Sucrose.	Tannin.	Ash.
Sour	1·064	16·8	0·43	1·40	9·32	0·96	0·14	0·5
Sweet	1·067	17·6	0·48	0·64	11·10	0·26	0·09	0·5

According to Hartman and Bullis (Oregon Agric. Exp. Sta. Bull. 1929, No. 247), the ripening of cherries is associated with an increase in sugar and non-sugar solids and a decrease in acidity, tannin content and astringency, values recorded being:

Date.	Acids (as malic). %	p_H.	Sugars. %	Non-sugar solids. %
June 23	0·75	3·68	7·4	3·4
Aug. 1 .	0·72	3·96	16·5	6·2

The sugars consist almost entirely of sucrose, glucose and fructose. Traces of inositol are present. The principal acid is malic acid, and there are very contradictory reports as to the presence of small amounts of succinic, citric and tartaric acids.

Traetta-Mosca *et al.* (Annali Chim. Appl. 1923, **13**, 333) have shown that unripe but not ripe fruit contain a peroxydase, invertase and emulsin being present at all stages of growth. The emulsin, according to Hofmann (Biochem. Z. 1934, **272**, 426), contains a large proportion of β-glucosidase and very little β-galactosidase.

The colouring matter of cherry skins has been characterised by Willstätter and Zollinger (Annalen, 1916, **412**, 164) as *keracyanin* (chloride, $C_{27}H_{31}O_{15}Cl$) yielding on hydrolysis with hydrochloric acid, cyanidin, glucose, and rhamnose. It thus appears to be a diglucoside of cyanidin, $C_{15}H_{10}O_6$.

König gives the composition of the ash as: K_2O 54·8, Na_2O 4·4, CaO 5·8, MgO 5·4, Fe_2O_3 1·5, Mn_3O_4 0·8, P_2O_5 15·6, SO_3 5·4, SiO_2 5·0, Cl 1·6 %.

The iron content of cherries appears to vary considerably with the type. Minor elements recorded by various analysts include: Al 34·9, Cu 1·6, Zn 1·5 mg. per kg. fresh weight.

The kernels of cherry stones average about a quarter of the weight of the stone and contain H_2O 6·3%, protein 28·0%, ether extract 38·7% (Alpers, Z. Unters. Nahr.-Genussm. 1917, **34**, 433).

A. G. Po.

CHERRY KERNEL OIL is the fatty oil present to the extent of 30–40% in the seed-kernels of the cherry, *Prunus Cerasus* L. Since 1926, attention has been paid in the United States to the recovery of the oil on a commercial scale from the kernels of the sour cherry, which are available as a by-product of the cherry-canning industry. About 34 tons was thus prepared in 1929, but the potential production of oil, assuming all the pips separated at the canning plants were utilised for this purpose, has been estimated at about 2,000 tons per annum. Refined cherry kernel oil is pale in colour and of a bland flavour, and the American product is reported to have good keeping properties. It resembles almond and apricot kernel oils in many respects and is similarly employed in the manufacture of cosmetic and pharmaceutical preparations; it is also suitable for use as a salad or culinary oil. The following figures have been recorded by Jamieson and Gertler (Oil and Fat Ind. 1930, **7**, 371) for a commercial specimen of refined American cherry kernel oil: d^{25} 0·9183, saponification value 190·7, iodine value (Hanus) 115·8, unsaponifiable matter 0·5%; the fatty acids consisted of 2·9% of stearic acid, 4·2% of palmitic acid, 49% of oleic and 42% of linolic acid, together with traces of myristic (?) and arachidic acids. Iodine values from 109 to 123 have been recorded by other observers for crude cherry kernel oils from various sources (*cf.* Alpers, Z. Unters. Nahr.-Genussm. 1917, **34**, 433; Spitaleri, Drug and Cosmetic Ind. 1936, **38**, 331; Tilgner, Konserven Ind. 1931, **18**, 257).

The oil gives orange or reddish colorations in the Bieber and Kreis tests (*see* ALMOND OIL). According to Rabak (U.S. Dept. Agric. Bull. 390, 1916; Oil and Soap, 1932, **9**, 210) fresh cherry kernels contain a glucoside of the type of *amygdalin*, about 1% of volatile oil, resembling essential almond oil (*q.v.*) being recoverable from the press-cake remaining from the expression of the fatty oil (the kernels from imported cherries, which had been preserved by treatment with sulphur dioxide and brine, however, did not have the characteristic " bitter almond " taste). The residual seed meal, after recovery of the fatty oil, could be used as a fertiliser, or, if freed from volatile oil (hydrocyanic acid) as an ingredient of cattle-food.

E. L.

CHERRY-LAUREL, ESSENTIAL OIL OF. Obtained by distillation of the leaves of *Prunus Laurocerasus* Linn. (Fam. Rosaceæ), a native of Persia, and cultivated generally as an ornamental shrub. The leaves contain a cyanogenetic glucoside *laurasin* which interacts with an enzyme yielding benzaldehyde and hydrocyanic acid. The oil separates from the distillation water with a yield of 0·05%.

Characters.—Sp.gr. 1·050 to 1·065, optical rotation −0° 30′ to +0° 30′. Contains about 98% of benzaldehyde. The distillation water is standardised to contain 0·1% of hydrocyanic acid, and is used in medicine under the name cherry-laurel water, principally in eye lotions.

C. T. B.

CHERRY-LAUREL LEAVES. *Laurocerasi folia* (B.P.); leaves of *Prunus Laurocerasus* Linn.

CHERT. A compact form of silica essentially the same as flint, differing from this mainly in its geological occurrence. The name flint is usually restricted to the nodules of irregular shape found in the chalk of Cretaceous age, whilst chert more often forms slabby masses, sometimes thick beds, in rocks of all geological periods. It is usually associated with limestones and dolomites, and sometimes a gradual passage can be traced between the two, suggesting that the beds of chert have been formed by the silicification (metasomatic replacement) of limestone. Fossils are also replaced by silica, but there are also often present sponge spicules and the siliceous tests of radiolaria. In the latter case the silica is of organic origin; while in others it has no doubt been deposited from solution as colloidal silica, which has later crystallised on a minute scale. The microcrystalline material consists of finely granular quartz and fibrous chalcedony, together with some opaline silica. The fracture of chert is more uneven and splintery and the broken surface less smooth than in typical flint.

The material varies considerably in appearance, ranging from white to black in colour, and sometimes with a cavernous texture. It also varies in chemical composition. Analyses by H. F. Harwood (Geol. Mag. 1923, **60**, 177) of chert from north Flintshire show SiO_2 94·45–97·83, Al_2O_3 0·36–2·42, Fe_2O_3 0–0·28, FeO 0–0·22, CO_2 0–2·72, C 0–0·60%. A collection of analyses of chert from American localities is given by W. A. Tarr (Univ. Missouri Studies, 1926, **1**, no. 2); one, from Joplin, Missouri, shows SiO_2 99·46, while a calcareous chert from Grand Falls, Missouri, shows SiO_2 63·67, $CaCO_3$ 32·12%.

Deposits of chert are worked at Bakewell in Derbyshire, Halkin in Flintshire, and Reeth in Yorkshire, and the crushed material is used in the production of pottery glazes, and for grinding and polishing. (H. C. Sargent, Geol. Mag. 1921, **58**, 265; 1923, **60**, 168; 1929, **66**, 399; W. A. Tarr, The Origin of Chert and Flint, Univ. Missouri Studies, 1926, **1**, no. 2; Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, vol. 6, Refractory Materials: ganister and silica rock, 2nd ed., 1920.)

L. J. S.

CHESSYLITE or AZURITE. Hydrated basic copper carbonate, $2CuCO_3{\cdot}Cu(OH)_2$, forming monoclinic crystals of an azure-blue colour. Finely crystallised specimens have been found in abundance in an old copper mine at Chessy, near Lyons, in the south of France, and on this account the mineral is often known as chessylite (Brooke and Miller, 1852); the name azurite (F. S. Beudant, 1824) refers to the characteristic colour. Sp.gr. 3·8; hardness 3½–4. It occurs as an alteration product of chalcopyrite and other sulphide ores of copper in the upper oxidised zones of mineral veins; and it is itself often altered to malachite, the green carbonate ($CuCO_3{\cdot}Cu(OH)_2$). Fine crystals are also found at Broken Hill in New South Wales, Tsumeb in South-West Africa, and at Bisbee in Arizona; at the last-named place it occurs, together with malachite, in sufficient abundance to be mined as an ore of copper. It was also formerly mined at Burra-Burra in South Australia. From Arizona come pretty specimens, with azurite and malachite banded together, which are polished for use in cheap jewellery. Powdered azurite was formerly used as a pigment under the name " mountain blue," but this is now replaced by an artificial product.

L. J. S.

CHESTNUT. Under the general title " chestnut " are included:

(1) The sweet chestnut, the seed of *Castanea sativa* Mill (or *C. vesca* Gaertn.), the European species, of the large American species, *C. dentata* Borkh., and of two smaller, dwarf-growing species, *C. pumila* Mill. and *C. alnifolia* Nutt. (the American chinquapins).

(2) The horse chestnut, the seed of *Æsculus Hippocastanum* L.

(3) The water or horn chestnut, the horned fruit of *Trapa natans* (European), of *T. bicornis* (Chinese), or of *T. bispinosa* (Indian).

(4) The Chinese water chestnut, which is the onion-shaped corm of *E leocharis tuberosa* Schult.

The sweet chestnut is eaten roasted, or skinned and minced as a dressing for poultry, etc., or in Italy is prepared as a flour and used for cooking.

The horse chestnut, although rich in nutrient material, has a bitter flavour which precludes its use as a human food. Auld (J.S.C.I. 1913, **32**, 173) records that the nuts are not markedly poisonous to animals and may be used in moderate proportions as a cattle food. Serger (Chem.-Ztg. 1916, **40**, 221) prepares a satisfactory cattle food by boiling the coarsely ground nuts with successive portions of water.

The starchy kernel of the horn chestnut or Jesuits' nut renders it serviceable directly as a food, or for the manufacture of a flour, or as a source of a commercial starch.

The corms of the true water chestnut are eaten either raw or cooked by the Chinese and may also be used for the preparation of starch.

The average percentage composition of these " chestnuts " (kernels) is :

	H_2O	Protein.	Fat.	N-free extract.	Reducing sugars.	Sucrose.	Starch.	Fibre.	Ash.
Sweet chestnut (dried)[1] . .	4·70	7·44	2·90	80·0	5·36	9·0	50·6	2·28	2·68
„ „ flour[2] . .	14·0	8·02	3·54	69·9	2·88	26·72	40·0	2·80	2·54
Horse chestnut (dried)[3] . .	2·22	12·08	6·26	74·45	2·51			2·13	2·86
„ „ „ [4] . .	2·6	8·9	6·3		4·4	11·0	38·7	2·3	2·7
Horn chestnut (fresh)[5] . .	84·6	2·37	0·18	11·39	2·25		9·14	0·4	0·8
Water chestnut (fresh)[6] . .	79·2	1·84	0·18	17·12				0·7	1·0

[1] Baker and Hulton, Analyst, 1918, **43**, 32.
[2] Leoncini and Manetti, Staz. sper. agr. ital. 1911, **44**, 66, 113.
[3] Quoted by Auld (*l.c.*).
[4] Baker and Hulton (*l.c.*).
[5] Brahmachari and Chatterjee, Indian Med. Gaz. 1927 **62**, 365.
[6] Adolph, Philippine J. Sci. 1926, **30**, 287.

In addition to the carbohydrate material cited above, Baker and Hulton record 5·09% pentosans in dried horse chestnut and 3·06% in sweet chestnuts. In water chestnut Hemmi has isolated a hemicellulose yielding *l*-arabinose on hydrolysis.

The bark, and to a small extent other parts, of the horse chestnut tree contains the glucoside æsculin (*q.v.*). Masson (Bull. Sci. Pharmacol. 1918, **25**, II 65) records the presence of æsculic acid (needles, m.p. 214°-215°) and æsculinic acid (yellow needles, m.p. 230°-231°, lævorotary) in the cotyledons. De Vevey (*ibid.* 1908, **15**, 696) describes a second glucoside, *argyrescin*, $C_{27}H_{42}O_{12}$, yielding glucose and *argyrin* on hydrolysis.

From the sweet chestnut Venezia (Ann. R. Ist. super agrar Portici, 1932, **5**, 136-139) isolated the polyalcohol *castagnitol*.

Kernels of the horse chestnut contain an oil somewhat resembling almond oil. Two available analyses give :

	d^{15}.	Sapon. value.	Iodine value.	Reichert-Meissl value.	Polenske value.	Hehner value.	Acetyl value.	Acid value.	Unsapon. matter.	Refractive index.	Analyst.
(*a*)	0·926	194·5	95·4	1·54		92·5	13·5			1·4747	Chaplet.[1]
(*b*)		175·5	99·0	1·01	0·42	92·8		11·67	2·50	1·4710	Heiduschka and Zeileis.[2]

[1] Rev. chim. Ind. 1913, **32**, 173.
[2] Z. Unters. Nahr.-Genussm. 1917, **33**, 446.

In an examination of protein constituents of the horse chestnut, Belozerski and Dubrovskaja (Biochimia, 1936, **1**, 665) isolated a globulin *hippocastanin*, and a nucleo-protein which on hydrolysis yielded amino-acids of similar composition to those from hippocastanin, and nucleic acid from which guanine, adenine, cytosine, thymine and lævulic acid were obtained. Colby gives the following analysis of the ash of sweet chestnut kernels: K_2O 48·7, Na_2O 1·2, CaO 4·6, MgO 8·1, Fe_2O_3 0·4, Mn_2O_3 0·2, P_2O_5 23·55, SiO_2 0·18, SO_3 12·8, Cl 0·34%. Small amounts of copper and zinc are also present.

A. G. Po.

CHESTNUT EXTRACT. The wood of the sweet or Spanish chestnut (*Castanea vesca*), though it contains only 3–6% of tannin, is the source of the much valued chestnut extract. The bark contains more tannin (17%) than the wood, but is not much used. The tree, which grows to a height of 60–80 ft., is abundant in Italy, the South of France and Corsica, where it forms immense forests, and it is also very common in America.

Freudenberg and Walpuski (Ber. 1921, **54**, [B], 1695) isolated the crude tannin and, by hydrolysis with dilute sulphuric acid, obtained a small amount of quercetin, traces of gallic acid, sugar (2%, chiefly dextrose), and ellagic acid (15–20%). All these are present in the combined form. No sugar was produced by the action of emulsin, thus indicating that quercetin and ellagic acid are not present as glucosides. Purification of the crude tannin was effected by the action of aspergillus-tannase, then precipitating with a lead salt and decomposing the precipitate with hydrogen sulphide. The purified tannin is a yellowish-red, strongly acidic substance, almost insoluble in ethyl acetate, and yields only 3% of ellagic acid when heated for 5 hours with 3% sulphuric acid. The acidity indicates a molecular weight of about 400 or some multiple thereof. It gives a blue coloration with iron salts, but is not precipitated by bromine water and does not contain phloroglucinol. Chestnut tannin thus appears to be a representative of a new type of tannin and to be closely allied to that of the native (German) oak.

Müller and Zellner (Biochem. Z. 1935, **277**, 383) describe the precipitation of a phlobaphene, empirical formula $C_{27}H_{20}O_{16}$, from chestnut tannin extract. When oxidised with alkaline peroxide, it yields a *product*, $C_{14}H_6O_8,2H_2O$, decomposing at 400°, which resembles but is not identical with ellagic acid. Distillation of the phlobaphene with zinc dust gives anthracene and naphthalene, but no fluorene, whilst by fusion with potassium hydroxide protocatechuic acid, succinic acid and pyrogallol are produced.

From the leaves of the *Castanea vesca*, Kurmeier (Collegium, 1927, 273) isolated a tannin from which, by hydrolysis, 8–9% of ellagic acid was obtained. The methylated tannin has the composition $C_{24}H_{12}O_8(OMe)_8$, and yields trimethyl citrate on distillation. Münz (*ibid.* 1929, 499) obtained 3·8% of a tannin, a galloylhexose, from the same source.

Chestnut is employed almost entirely in the form of extract, the strength of which varies, but usually contains from 26 to 32% of tannin. The extract is frequently decolourised, and sometimes mixed with quebracho extract and other materials. Chestnut tannin is the tannin which is most largely employed for the dyeing of silk. *Castanea vesca* appears to be frequently confused with the horse-chestnut, *Æsculus Hippocastanum.* The tannin derived from this latter is, however, of little or no practical value (*cf.* Pollak, Collegium, 1913, 291).

A. G. P. and E. J. C.

CHIAN TURPENTINE. A turpentine derived from *Pistacia Terebinthus* Linn.

CHIASTOLITE *v.* ANDALUSITE.

CHICA RED and CARAJURA. These are rare pigments prepared by the Indians of Central America from species of *Bignonia* which are very similar in appearance and may contain as a basis the same colouring matter. According to Crookes ("Dyeing and Calico Printing," 1874, p. 388) chica is obtained from the leaves of the *Bignonia Chica,* which the Indians boil with water, and add some particles of the bark known as "aryane" to the decanted liquid, which causes the precipitation of the colouring matter. An interesting résumé of what is known of chica and similar preparations is given by Holmes (Pharm. J. 1901, **12**, 595). Lee (J.C.S. 1901, **79**, 284) describes the preparation of a pigment from the heartwood of *Bignonia Tecoma.*

Erdmann (Jahresber. 1857, 487) isolated a colouring matter from an alcoholic extract of a specimen of chica red said to be derived from the leaves of the *B. chica,* and assigned to it the formula $C_8H_8O_3$.

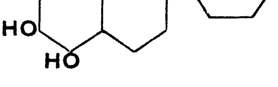
The colouring matters present in carajura have been studied by Perkin (Proc. Chem. Soc. 1914, **30**, 212) and Chapman, Perkin and Robinson (J.C.S. 1927, 3015). The sample consisted of dull red fragments possessing a peculiar camphoraceous odour, was insoluble in water, alcohol and dilute alkalis, and contained approximately 4% of colouring matter as calcium or magnesium lake, 23% of peaty matter, perhaps "aryane," a wax, and a resin in small relative amount. The mineral matter as ash (38%) consisted mainly of lime, magnesia and silica, together with some potassium carbonate.

The powdered carajura, after boiling with benzene to remove wax, and digestion with dilute hydrochloric acid at 95°, was extracted with boiling alcohol. The residue obtained on evaporation was digested with boiling benzene, by which means *carajurin,* the main colouring matter, was isolated. Subsequent extraction of the residue with boiling acetone yielded a second colouring matter, *carajurone,* as an indistinctly crystalline scarlet mass.

Carajurin, $C_{15}H_7O_2(OH)(OMe)_2$, garnet needles, m.p. 205°–207°, is sparingly soluble in hot benzene and alcohol, more readily so in pyridine. It dissolves sparingly in dilute aqueous caustic alkalis to orange-red solutions which become brown on keeping, but does not dissolve in boiling dilute aqueous ammonia (distinction from carajuretin). With alcoholic lead acetate carajurin gives a solution which slowly deposits pale red needles, whereas alcoholic ferric chloride gives a brownish-violet solution which becomes brown on the addition of an excess of the reagent. Well-defined, crystalline, orange-red oxonium salts are obtained with acids, and from these the base is easily recovered. Bromination of carajurin yields a *compound,* $C_{17}H_{12}O_5Br_4$ or $C_{17}H_{14}O_5Br_4$, orange needles, which is apparently both a hydrobromide and a perbromide; on treatment with boiling acetone it is changed into *dibromocarajurin,* $C_{17}H_{12}O_5Br_2$, bright red needles. These bromo-derivatives do not melt, but become carbonaceous powders at 300°.

In many respects carajurin resembles the anhydrohydroxybenzopyranol bases prepared by Bülow and his collaborators. The coloured anhydrohydroxybenzopyranols have frequently been found to yield colourless derivatives of hydroxybenzopyranols, and by acetylation of carajurin a colourless *triacetyl* derivative, m.p. 142°, of hydrated carajurin is obtained. Further, fusion of carajurin with caustic alkali affords *p*-hydroxybenzoic acid, whilst by boiling with concentrated aqueous potassium hydroxide, *p*-acetylanisole is produced.

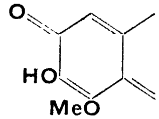
Demethylation of carajurin with hydriodic acid gives *carajuretin hydriodide,* $C_{15}H_{11}O_5I$, which has the composition and properties of a tetrahydroxyflavylium iodide. Its constitution was established by the synthesis of scutellareinidin chloride:



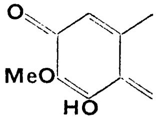
which proved to be identical with carajuretin hydrochloride.

The action of cold pyridine on carajuretin hydriodide leads to the formation of *carajuretin*, $C_{15}H_{10}O_5$, scarlet needles which become black at 330° without melting. With acetic anhydride and pyridine in the cold a colourless *penta-acetyl* derivative, m.p. 156°–157°, of hydrated carajuretin is obtained.

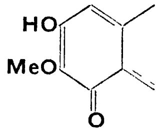
In considering the structure of carajurin there are four possible arrangements differing only in the position of the substituents in the trihydroxybenzene nucleus:



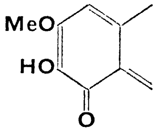
I.



II.



III.



IV.

Of these (II) and (III) are tautomeric and would yield the same hydrochloride. The synthesis of this hydrochloride, however, proved that it was not identical with carajurin hydrochloride. The choice between (I) and (IV) cannot yet be made definitely, but (I) is preferable on account of the colour and stability of carajurin.

Carajurone, m.p. 183°–186° (decomp.), dissolves in aqueous sodium carbonate to a brownish-red solution, the colour of which is neither so intense nor so persistent on dilution as that obtained from carajurin under similar conditions. The ferric chloride reaction closely resembles that given by carajurin; alcoholic lead acetate gives a maroon-coloured precipitate. The substance combines with strong acids forming oxonium salts, and there can be little doubt that it is a carajuretin monomethyl ether. The perceptible odour of *p*-acetylanisole observed on boiling a solution of carajurone in concentrated aqueous sodium hydroxide indicates that the methoxyl is in position 4′.

Dyeing Properties.—Carajurin and carajurone dye mordanted fabrics in almost identical shades, whereas those given by carajuretin are somewhat yellower. The following comparative results were obtained on mordanted wool:

	Chromium.	Aluminium.	Tin.	Iron.
Carajurin . .	Deep maroon	Dull brownish-red	Bright scarlet	Deep violet-maroon
Carajurone .	Deep maroon	Dull brownish-red	Dull scarlet	Deep violet-maroon
Carajuretin .	Brown	Dull brownish-orange	Brownish-scarlet	Brownish-maroon

A. G. P. and E. J. C.

CHICK PEA. An annual legume, *Cicer arietinum*, extensively grown in India, where it is known as Bengal grain, and in the Mediterranean countries. The seeds form a valuable food for cattle, or, after removal of the husks, for man. They are boiled and eaten as a vegetable or in some countries are roasted and used as a coffee substitute. A preparation of roasted chick peas forms an important food substance (*Lebleliji*) in Bulgaria. In India the young leaves are sometimes fried in oil.

The chick pea plant differs from the majority of common pea species in possessing numerous glandular hairs which secrete acid material consisting mainly of citric, malic and oxalic acids (G. R. Milne, J. Roy. Tech. Coll., 1934, **3**, 330).

Average analyses of chick peas and of *Lebleliji* by Zlataroff and Stoikov (Z. Unters. Nahr.-Genussm. 1913, **26**, 242) are:

	H_2O.	Protein.	Fat.	N-free extract.	Starch.	Fibre.	Ash.
Chick peas	10·47	22·6	5·08	56·14	49·33	3·09	2·88
Lebleliji .	6·14	24·8	6·09	58·0	57·99	2·21	2·73

The composition of the dry matter of stems, leaves, and seeds according to Passerini (Staz. sper. agr. ital. 1891, **21**, 20) is: (as percentages):

	Protein.	Fat.	Cellulose.	Other carbohydrates.	Ash.	Nitrogen.
Stems	6·35	1·8	35·0	49·0	7·81	1·62
Leaves	14·21	4·1	13·9	58·9	8·83	2·27
Seeds	26·20	5·2	1·7	63·6	3·30	4·19

The nitrogen distribution of seeds examined by Zlataroff (Z. Unters. Nahr.-Genussm. 1916, **31**, 180) is given as: total nitrogen 3·34, protein nitrogen 2·11, nuclein nitrogen 0·10, ammoniacal nitrogen 0·10, peptone nitrogen 0·007, amido-nitrogen 0·01, amino-nitrogen 0·12. Ivanov (Bul. Appl. Bot. Leningrad, 1933, III, No. 1, 3) observes a very wide range of protein content depending on growth conditions. Extreme values were 12·3% and 31·5%, the lowest occurring in soils from which the specific nodule bacteria were absent. The composition of the globulin of chick peas is shown by Narayana (J. Indian Inst. Sci. 1930, **13**, A, 153) to be:

	%
Cystine	0·88
Tyrosine . . .	4·90
Tryptophan . .	0·41
Arginine . . .	10·3 (van Slyke) 12·1 (direct)
Lysine . . .	7·6
Histidine . . .	1·0

Small amounts of adenine, betaine, and choline were detected by Zlataroff, who also records the nature of the phosphorus compounds as:

	%
Protein—P_2O_5 .	0·486
Lecithin . . .	0·142
Soluble organic .	0·244
Inorganic . . .	0·118
Total P_2O_5 . .	0·998

The seeds also contain appreciable amounts of inosite and phytin.

The fat present in the seeds has the following characteristics: sp.gr. at 15° 0·9396–0·9376, solidifying point −19·5°, n_D^{25} 1·4744, saponification value 240, the acid number of the crude fat is 0·3 to 0·5, iodine value 110–119, Reichert-Meissl value 4·51, Polenske value 1·1, Hehner value 91·6, ester value 239·5, unsaponifiable matter 0·48%. The separated fatty acids have m.p. 25°, iodine value 129.

Zlataroff (*l.c.*) records the presence of 0·3% of a sterol *slanutosterol* (acetate, m.p. 128°). Passerini (*l.c.*) gives the composition of the ash as: K_2O 24·6, Na_2O 1·29, CaO 4·45, MgO 19·98, Fe_2O_3 2·42, P_2O_5 39·56, SO_3 3·38, SiO_2 2·85, and Cl 0·71%.

A. G. Po.

CHICLE. Chicle or chicle gum, as it is often termed, is the thickened latex of a Mexican tree, *Achras Zapota*. It is used to a considerable extent in the manufacture of chewing gum. The commercial article is a mixture of water-soluble gums resins, and mineral matter. Prochazha and Endemann (Pharm. J. 1879, **9**, 1045, 1065) give the following analysis of a clean sample of chicle:

	%	
Soluble in water . .	25·00	(gum and mineral salts)
Alban	33·75	
Fluavil	22·50	
Hydrocarbons soluble in ether . . .	6·00	
Hydrocarbons insoluble in ether	12·75	

E. J. P.

CHICORY. *Cichorium Intybus.* In addition to the widespread use of the ground roasted root for admixture with coffee, the green plant itself forms a serviceable food, and the young green leaves, blanched by growing in cellars or by covering with soil in the open, are used raw as a salad or boiled and eaten as a vegetable—the French endive.

Complete analyses of chicory are seldom reported; the majority of published data relates to partial analyses, which may serve to determine the composition of coffee-chicory mixtures or for the detection of common adulterants, *e.g.* ground sugar beet or artichoke. Wynter Blyth quotes the following for fresh roots:

Water.	Gummy matter.	Glucose.	Bitter extractive.	Fat.	Cellulose inulin and fibre.	Ash.
%	%	%	%	%	%	%.
77·0	7·5	1·1	4·0	0·6	9·0	0·8

Earlier analyses by Mayer (Bied. Zentr. 1885, 828) give:

Water.	Albuminoids.	Fat.	Inulin.	Fibre.	Sugar.	Bitter extract.	Ash
%	%	%	%	%	%	%	%
72	1·1	0·2	12·0	1·4	5·6	0·5	1·4
to			to	to	to	to	to
77			17·3	1·8	6·0	0·15	1·9

During the roasting process there is considerable destruction of inulin and the roasted product contains increased proportions of reducing sugars together with dextrin and caramel. Petermann found pure roasted chicory to contain:

Water-soluble material (74·2%).

Water.	Glucose.	Dextrin and inulin.	Protein.	Colouring matter.	Ash
%	%	%	%	%	%.
16·3	26·1	9·6	3·2	16·4	2·6

Water-insoluble material (25·8%).

Protein.	Fat.	Cellulose.	Ash.
%	%	%	%
3·2	5·7	12·3	4·6

An approximate determination of the composition of mixtures of coffee and chicory may be made, according to Leebody, on the basis that the tinctorial power of chicory is roughly three times that of coffee.

The characteristic odour of roasting chicory has been examined by Reichstein and Beitter (Ber. 1930, **63**, [B], 816), who record that the volatile matter produced contains acetaldehyde, acetone, diacetyl, βγ-diketopentane, furfuraldehyde, 5-hydroxymethyl-furfuraldehyde, maltol, furan, methyl and furfuryl alcohols, acetic, pyruvic, lactic, pyromucic and palmitic acids, together with traces of phenols and a neutral oil. These substances may be regarded as derived from carbohydrate materials. The large proportions of furfuraldehyde and hydroxymethyl furfuraldehyde which are derived from inulin, together with the absence of volatile nitrogen and sulphur compounds, form a marked contrast with the products obtained during the roasting of coffee. Hehner and Skertchly have suggested the determination of furfuraldehyde (as a measure of pentosans) for detecting the presence of chicory in coffee. The pentosan content of coffee is 5·0–5·5%, and that of chicory 2·5% (Analyst, 1899, **24**, 178).

During storage of chicory roots inulin is partially converted into inulide, and possibly into other more easily fermentable products. Wolff and Geslin indicate the presence in the roots of an enzyme which effects the transformation: inulin → inulide → fructose (Compt. rend. 1917, **165**, 651; 1918, **166**, 428). This change may be brought about in a quantitative manner by heating at 80°–100°, or in an autoclave, with appropriate amounts of mineral acid, (Bobkov, Z. Spiritusind. 1936, **59**, 97, 239, 247). In another investigation Wolff (Compt. rend. 1916, **164**, 514) records that the roots contain a substance (probably an enzyme) which he terms *inulo-coagulase*, which coagulates inulin in the expressed juice. Its action is apparently specific for inulin.

The bitter principle of chicory is probably a glucoside of fructose and pyrocatechuic aldehyde (Grafe, Biochem. Z. 1915, **68**, 1). Zellner and Richling (Monatsh. 1926, **47**, 695), in examining the juice of roots, give the formula $C_{18}H_{20}O_6$ to the bitter substance, and also report the presence of a stearin, mannite and tartaric acid. Wolff also described (1899) an optically inactive sugar which he named *synanthrose*. Grafe (Beitr. Biol. Pflanz. 1935, **23**, 336) states that a glucoside occurs in chicory in which inulin functions as the carbohydrate.

Betaine and choline occur in small amounts in chicory and are not affected by the roasting process. Adulteration of chicory with sugar beet (which contains approximately seven times the quantity of betaine) is thus easily detected (Vondrak, Zentr. Zuckerind Czechoslov. 1929, **53**, 366). A microscopical method for this purpose is based on the occurrence of crystals of calcium oxalate in certain cells of sugar beet examined after removal of colouring matter by repeated washing with sodium hypochlorite solution (Collin, Ann. Falsif. 1916, **9**, 271).

The presence of chicory in coffee may be ascertained by determination of the cupric-reducing power of the extract. Roasted coffee contains 1·9–2·6% and roasted chicory 25–27% of reducing sugars.

The sp.gr. of extracts also offers a means of detecting adulteration in many cases as the following values for the sp.gr. of infusions of various materials with ten times their weight of water indicate:

Spent tan	1·00214
Acorns	1·00730
Peas	1·00730
Mocha coffee	1·00800
Ceylon coffee	1·00870
Java coffee	1·00870
Costa Rica coffee	1·00900
Native Ceylon coffee . . .	1·00900
Brown malt.	1·01090
Black malt	1·02120
Dandelion root	1·02190
Red beet	1·02210
Yorkshire chicory . . .	1·01910
Foreign chicory	1·02260
Guernsey chicory	1·02326
Maize	1·02530
Bread raspings	1·02630

(quoted by Wynter Blyth, "Foods," p. 360).

The percentage composition of the ash of chicory roots and leaves is as follows:

	K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Root	40·4	7·7	6·3	8·7	3·0	14·2	9·0	6·0	3·7
Leaves	60·0	0·7	3·2	14·3	—	9·0	9·0	1·0	1·7

Wynter Blyth (" Foods," pp. 359, 1909) gives as the main differences between the ash of coffee and of chicory, the following:

	Coffee ash. %	Chicory ash. %
Silica and sand . .	—	10·7–35·9
Carbon dioxide . .	14·9	1·8–3·2
Ferric oxide . . .	0·44–0·98	3·1–5·3
Chlorine	0·26–1·1	3·3–4·9
Phosphorus pentoxide	10·0–11·0	5·0–6·0
Soluble ash . . .	3·0	1·74

A. G. Po.

CHILE SALTPETRE. *Sodium nitrate.*

CHILLIES *v.* CAPSICUM.

CHINA CLAY or KAOLIN *v.* CLAY.

CHINA GRASS. *Ramie, Rhea.* This fibre is obtained from the stem of a plant of the Urticaceæ, which grows to the height of 4–8 ft. and in general character resembles the common nettle, *Urtica dioica* Linn., but is devoid of stinging hairs. The plant exists in two varieties, (1) *Boehmeria nivea* Gaudich., which bears short, silvery hairs on the lower surface of the leaves, and (2) *B. nivea* var. *tenacissima*, the leaves of which are green on both sides. The former variety is cultivated chiefly in China and Formosa under the name of " ch'ü-ma " or " tchou-ma," whilst the latter occurs in more tropical countries, such as the islands of the Malay Archipelago, where it is known as " rhea." The Indian form has been sometimes regarded as *B. nivea* var. *tenacissima*, but Sir George Watt affirmed that it is of the same variety as the Chinese plant. The cultivation of the plant in China is carried on chiefly in the valleys of the provinces of Hunan, Hupeh, Kiangsi, and Szechuen.

The fibre resides in the inner bark or bast tissue of the stem. The methods of extraction differ widely from those used in the case of flax and hemp as the encrusting substances are not removed by a retting process but by chemical means. The commercial " China grass " is prepared in China by hand. The bark is peeled from the stems and the outer brown skin or pellicle removed from it by scraping and washing. The process is tedious, the production of a few pounds of the scraped ribbons constituting a day's work. In these ribbons the fibres are firmly embedded in a gummy substance of a pectinous nature which must be removed to obtain the " filasse " or pure fibre ready for spinning. This operation, termed " degumming," is not carried out before export, but is effected subsequently by chemical treatment. The process is designed to dissolve and wash out the gummy substances without attacking the cellulose ; at the same time, the fragments of brown pellicle still adhering become detached and are removed by washing. On account of the danger of the fibre becoming injured by the degumming treatment, spinners usually prefer to buy the fibre in the form of ribbons of hand-cleaned China grass and degum it by their own process. Many different processes have been devised and are usually guarded as trade secrets. The following will, however, serve to indicate the kind of treatment to which the material is subjected. The ribbons, after boiling in dilute caustic soda, are exposed to the action of a solution of bleaching powder, and then immersed in a bath of dilute acid, the last two processes being repeated until the whole of the gum has been extracted and the white, lustrous filasse obtained.

Yield.—From two to four or even six cuttings of ramie stems can be obtained annually according to the climatic and other conditions of the locality in which the crop is grown. It is estimated that from two cuttings the yield of fresh stems per acre amounts to 15–20 tons, giving ¾–1 ton of dry scraped ribbons. The ribbons furnish about 50% of their weight of degummed fibre or filasse, and hence the yield of filasse per acre amounts to approximately 7½–10 cwt. per annum.

Characters, Uses and Composition.—Ramie fibre is one of the strongest known. It is extremely durable and is said to be less affected by moisture than any other fibre, but it is somewhat lacking in elasticity. The fibre has a brilliant, silky lustre, can be dyed readily, and is exceptionally long. The filasse consists of isolated ultimate fibres or small groups of fibres. The ultimate fibres vary from 75 to 400 mm. in length and from 0·02 to 0·075 mm. in diameter, the average diameter being about 0·0375 mm. or about twice as great as that of cotton fibre. The fibres taper towards each end, but the ends themselves are rounded. They are thick-walled, have a well-marked lumen, and bear longitudinal striations and occasional transverse markings. The fibre substance consists of non-lignified cellulose.

It has been suggested as the result of a study of ramie by X-ray methods that the ultimate fibres are composed of chains of long, thin, submicroscopic crystals which lie roughly parallel to the fibre axis. These crystals are estimated to be approximately $0{\cdot}075\mu$ long and $0{\cdot}005\mu$ thick (*see* W. T. Astbury, "Fundamentals of Fibre Structure" (1933), and G. F. Davidson, J. Text. Inst. 1936, 27, P144).

China grass is used extensively in China for the manufacture of fabrics known as "grass-cloths." In Europe the fibre is woven into goods of various descriptions, such as lace, curtains, tablecloths, counterpanes, plushes and even clothing materials. It has been used successfully in combination with wool for the production of certain classes of fabrics and has also found an outlet in the manufacture of mantles for incandescent gas-lighting.

E. G.

CHINA INK or *Indian Ink* consists of lampblack made into a paste with animal or fish glue and dried in the form of cakes or sticks of paint.

CHINA-STONE. A granitic rock having its felspathic constituent more or less decomposed, but not completely kaolinised, and with an absence of coloured minerals, such as biotite and tourmaline. As the felspar still retains part of its alkali, and as some micaceous mineral is generally present, the stone is fusible ; hence it is largely used in the manufacture of porcelain, and when free felspar is not introduced it forms the only vitrifiable constituent of the paste. China-stone is sometimes known as "Cornish stone" in consequence of its being largely quarried in Cornwall, where it was discovered by W. Cookworthy of Plymouth, about 1750. He first noticed it at Tregonning Hill, near Breage, and described it under the local name of "growan" or "moor-stone." It is now obtained principally from the neighbourhood of St. Stephens near St. Austell. In this area it occurs as a local modification of the granite, and is sharply marked off from the normal granite and from the china-clay rock. It is too hard to be worked like the china-clay rock, and has to be blasted and quarried like ordinary granite; in fact it has been used locally as a building stone. The rock requires no preparation, but is sent direct from the quarry to the potteries. (For an account of the occurrence of china-stone in Cornwall, *see* Mem. Geol. Survey, Bodmin and St. Austell district, 1909; and the Handbook by J. A. Howe, quoted below.)

The following commercial varieties are recognised:

1. "Hard purple," a hard, white rock with a faint purplish tinge due to the presence of fluorspar.
2. "Soft" or "mild purple," similar to the last, but softer.
3. "Dry white stone," a soft, white variety.
4. "Buff stone," similar to the last, but iron stained.

The following analyses by W. Pollard and E. G. Radley are given by J. A. Howe, "A Handbook to the Collection of Kaolin, China-clay and China-stone in the Museum of Practical Geology," London, 1914. I. "Hard purple" china-stone from Goonvean, near St. Stephens; II. "Buff" china-stone from the same locality; III. China-stone from Jersey ("Jersey stone").

	I.	II.	III.
SiO_2 . . .	72·28	73·18	77·06
TiO_2 . . .	0·05	0·06	0·08
Al_2O_3 . . .	14·90	16·13	12·22
Fe_2O_3 . . .	0·50	0·52	0·47
MnO . . .	0·01	0·02	0·19
MgO . . .	0·15	0·14	0·19
CaO . . .	1·66	0·61	0·16
Na_2O . . .	3·01	2·18	3·23
K_2O . . .	5·25	4·41	5·07
Li_2O . . .	0·02	0·02	trace ?
H_2O (over 105°)	0·68	1·81	0·37
H_2O (at 105°) .	0·13	0·20	0·39
P_2O_5 . . .	0·53	0·45	0·25
F	0·88	0·23	FeS_2 0·30
Cl	0·09	—	CO_2 0·04
	100·14	99·96	100·02

Jersey stone is a decomposed partly kaolinised granite quarried in Jersey. Granite-pegmatite in France ; granite-aplite at Meldon, near Okehampton, Devonshire; porphyrite in Saxony; liparite in Japan; and felsite in China are all rocks that are applied for the same purpose.

It has been proposed by J. H. Collins ("Hensbarrow Granite district," Truro, 1878) to distinguish china-stone under the name *petunzite*, a word suggested by the Chinese *pe-tun-tse*. In the early part of the 18th century a Jesuit missionary named D'Entrecolles, residing at King-te-chin, sent to Réaumur, in Paris, samples of the raw materials used in China. These were the first specimens of their kind that had ever reached Europe, and they led to the foundation of the manufacture of porcelain at Sèvres. The china-stone was described by D'Entrecolles as pe-tun-tse, and the china-clay as kaolin; but it appears that the former name, if not both, must have been erroneously applied. According to the Chinese scholar, Stanislas Julien (Hist. et Fabric. de la Porcel. Chin. Paris, 1856, preface xx.), *pe-tun* signifies "white paste," while *tse* is merely a diminutive applied to the material when worked up into small cakes. Hence, *pe-tun-tse* is really the name of small blocks of white clay or prepared paste, and not of the granitic rock. Nevertheless, custom in this country has justified the use of the term *pe-tun-tse* as synonymous with china-stone.

L. J. S.

CHINA WOOD OIL, *nut oil,* synonyms for *tung oil.*

CHINAPHENIN, QUINAPHENIN. Quinine carbophenetide,

$$C_{20}H_{23}ON_2{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt.$$

CHINEONAL. Quinine diethylbarbiturate. Sedative and antipyretic.

CHINESE BLUE. (Ger., *Porzellanblau.*) Several pigments are sold under this name, of which the following are examples: ultramarine and flake white; cobalt blue and white lead; and a double cyanide of iron (Prussian blue).

CHINESE GREEN or LOKAO *v.* LOKAO.

CHINESE RED *v.* AUSTRIAN CINNABAR.

CHINESE VEGETABLE TALLOW, Stillingia tallow, is the hard fat which coats the seeds of the Chinese tallow tree, *Stillingia sebifera* Michx. (syn. *Stillingia sinensis, Croton sebiferus* L., *Sapium sebiferum* Roxb., *Excœcaria sebifera* F. Müll. Fam. Euphorbiaceæ), a tree growing wild, and also largely cultivated, in China, Indo-China and Northern India. Plantations have recently been developed in Florida and Texas. In Tonkin, the tree is also valued for its leaves, from which a decoction is prepared for dyeing silk. The fruit capsule contains three oval seeds surrounded by a mass of the true vegetable tallow. This "tallow" is to be distinguished from the oil obtained from the seeds (kernels) themselves, known as stillingia oil or locally as "tsé-tiéou" or "ting-yu," which is a liquid drying oil. The tallow may be scraped off the seeds by passing them between fluted rollers, or may be melted off by steaming the seeds in perforated cylinders. The product is pressed into cakes in native hot presses, and sold under the Chinese name of "pi-iéou" or "pi-yu," and is known in Europe as "prima vegetable tallow." According to another process, the seeds and tallow are crushed together, giving a mixture of the tallow and stillingia oil, known as "mou-iéou" or, to European candlemakers, as "secunda vegetable tallow"; this product is naturally much softer and has a lower melting-point and much higher iodine value.

When fully developed, the tree yields 25–30 kg. of fruit a year; the fruit yields about 30% of secunda or 15% of prima tallow. The cake is not suitable for cattle food, as it contains a saponin; in China it is used as a fuel.

The properties of the tallow vary considerably according to the source. The refractive index is 1·4546–1·4556 at 40°; the saponification value varies from 197 to 215, and the iodine value from 19 to 32. Considerable quantities of free fatty acids may be present; thus Hilditch and Priestman (J.S.C.I. 1930, **49**, 397) found as much as 25% in a specimen from the United States. They analysed this sample, and also two less pure Chinese specimens, and found the fatty acids to consist of 57–69% palmitic, 21–34% oleic, 3–6% myristic, and 1–3% stearic acids. The tallow contained about 25–35% of fully saturated glycerides (largely tripalmitin), and over 60% of mono-oleo-di-saturated glycerides (chiefly oleo-dipalmitins).

The solidification temperature appears to vary greatly, being usually about 38°C., but samples, probably impure, have been stated to solidify at 24°C., whilst the American sample examined by Hilditch set at 48·2°C.

Exports of Chinese vegetable tallow from Hankow to Europe and the U.S.A. amounted to 5,000–6,000 tons in 1923-25, but have greatly diminished since that time, and none has been imported into England for some years prior to 1938. A large proportion of the production is consumed in China for the manufacture of candles; the total exports from Hankow were 17,800 tons in 1917, and 8,200 tons in 1931. In Europe vegetable tallow was chiefly used in the candle and soap industries; its value as a confectionery fat is uncertain (*cf.* Diedrichs, Z. Unters. Nahr.-Genussm. 1914, **27**, 132).

J. L. and E. L.

CHINESE YELLOW (*King's yellow*). A mineral pigment owing its colour to the presence of hydrated ferric oxide.

CHINIOFON. Iodohydroxyquinoline-sulphonic acid mixed with sodium bicarbonate; antiseptic for the treatment of amœbic dysentery.

CHINOFORM. Trade name for quinine formate.

CHINOSOL or QUINOSOL. Trade name for the potassium salt of 8-hydroxy-quinoline-5-sulphonic acid,

$$C_9H_6NO{\cdot}SO_3K,H_2O,$$

a pale-yellow crystalline powder with a saffron-like smell and a burning taste; m.p. 175°–177·5°; readily soluble in water, sparingly soluble in alcohol, insoluble in ether; with ferric chloride gives an intense green colour, yellowish needles with copper salts, and a white precipitate with barium chloride. At a concentration of 1 in 1,000 its solutions possess as great a bactericidal action as mercuric chloride solutions of the same strength. An antiseptic and disinfectant.

CHINOTROPIN or QUINOTROPIN. Trade name for urotropine quinate.

CHINOVOSE *v.* CARBOHYDRATES.

CHINQUAPINS *v.* CHESTNUT.

CHIOLITE. A double fluoride of aluminium and sodium, $3AlF_3{\cdot}5NaF$, closely akin to cryolite [$AlF_3{\cdot}3NaF$], but crystallising in the tetragonal system. Found at the Ilmen Mountains in the southern Urals and with cryolite in Greenland.

L. J. S.

CHIOS TURPENTINE RESIN. The name Chios turpentine is, properly, restricted to the oleo-resin from species of *Pistacia*, although turpentine from some of the larches is often termed Chios turpentine. It is similar in character to ordinary turpentine oleo-resin. Emmanuel (Pharm. Acta Helv. 1935, **10**, 12) isolated from the resin of *Pistacia Terebinthus*, terminthic acid, $C_{14}H_{20}O_2$, m.p. 136°–137°; terminthinic acid, $C_{16}H_{24}O_4$, m.p. 124°; termintholic acid, $C_{13}H_{23}O_4$, m.p. 102°; and termintholinic acid, $C_{22}H_{34}O_3$, m.p. 128°. These acids have not yet been characterised by the preparation of crystalline derivatives.

Chios turpentine is variable in composition, and its characters depend entirely on the relative proportions of essential oil and resin.

E. J. P.

CHIRETTA. *Chirata*, B.P. Is the plant *Swertia Chirata* Buch.—Ham. collected when in flower and dried. Japanese chiretta is *Swertia chinensis* Franchet. Höhn (Arch. Pharm. 1869, 215) found two bitter constituents in Indian chiretta, viz. chiratin and ophelic acid.

CHITENINE, QUITENINE. An oxidation product of quinine, found in the urine after the administration of quinine. Crystallises from dilute alcohol in prisms, m.p. 281°–282°, $[\alpha]_D^{17}$ $-122{\cdot}6°$.

CHITIN. $[\alpha]_D$ $-14{\cdot}7°$ (in conc. HCl). Is a polysaccharide containing nitrogen which forms part of the skeletal substance of insects and crustaceæ; it is also an important skeletal element in the fungi. It is not possible to distinguish between animal and vegetable chitin by total nitrogen or by X-ray analysis; their chemical identity has been shown by Zechmeister and Tóth (Z. physiol. Chem. 1934, **223**, 53).

Chitin is extremely resistant to hydrolysis, but on boiling with concentrated hydrochloric acid it is converted into 1 mol. of glucosamine (2-aminoglucose) together with 1 mol. of acetic acid.

It is considered by Meyer and Mark (Ber. 1928, **61**, [B], 1936) to be built up of *N*-acetylglucosamine units in β-glucosidic linkages exactly as in cellulose.

Karrer and Hoffman state that an enzyme from the vineyard snail is able to hydrolyse chitin (Helv. Chim. Acta, 1929, **12**, 616, 986), the end product being acetylglucosamine.

By acetolysis of chitin with acetic acid in sulphuric acid, Bergmann *et al.* (Ber. 1931, **64**, [B], 2436) obtained the octa-acetate of a disaccharide chitobiose.

Zechmeister and Tóth (Ber. 1931, **64**, [B], 2028; 1932, **65**, [B], 161, 1706) obtained in addition a chitotriose and an amorphous water soluble chitodextrin.

The Röntgen diagram (Meyer, Helv. Chim. Acta, 1935, **18**, 589) also confirms the structure as being of the long chain cellulose type. It is not known whether the glycoside linkage is α or β.

E. F. A.

CHITINASE, the enzyme which hydrolyses chitin, was discovered by Karrer and Hoffmann (Helv. Chim. Acta, 1929, **12**, 616) in the digestive juices of *Helix*. It attacks genuine chitin only slowly, but after solution in concentrated hydrochloric acid, and separation by pouring into water, the chitin is easily hydrolysed. *N*-Acetylglucosamine is the final product alike from chitin of animal and fungal origin; chitodextrins are intermediate products. Chitinase is not the same as emulsin; it has, however, been obtained from the outer part of almonds free from β-glucosidase (Grassmann, Ber. 1934, **67**, [B], 1; Helferich, Z. Physiol. Chem. 1933, **221**, 253).

It has also been obtained from *Aspergillus oryzae* and is obviously widely distributed. The optimal p_H is 5·2; it is destroyed at 70°. Perhaps it is a mixture of two enzymes acting in succession.

Chitinase is able to hydrolyse synthetic glycosides of *N*-acetylglucosamine, for example, phenyl *N*-acetylglucosaminide. It is quite without action on the non-acetylated compound; chitosan is only hydrolysed as far as the polyglucosamine stage, whereas acetylchitosan is totally hydrolysed by the enzyme. The acetyl group is thus essential for the enzyme to be active; it cannot be replaced by formyl or benzoyl.

E. F. A.

CHITOSAMINE is glucosamine (2-aminoglucose) (*v.* CHITIN).

CHIVES. *Allium Schoenoprasum*, L. A perennial plant occurring naturally in many parts of Europe and cultivated for the round onion-like leaves which are used for flavouring. The percentage composition of the leaves is given as:

Water.	Protein.	Fat.	N-free extract.	Fibre.	Ash.
91·2	2·6	0·33	3·09	1·48	1·28

Churg and Ripperton (Hawaii Agric. Exp. Stat. Bull. 1929, No. 60). The mineral constituents include Ca 0·048, Fe 0·0084, and P 0·057%.

A. G. Po.

CHLOANTHITE. Native nickel arsenide, $NiAs_2$, isomorphous with smaltite ($CoAs_2$) there being no sharp line of demarcation between the two species. Found as cubic crystals and compact masses at Schneeberg in Saxony and Riechelsdorf in Hesse, where it was formerly mined as an ore of nickel. It occurs in considerable amount with silver ores at Cobalt and South Lorrain in Ontario.

L. J. S.

CHLORAL, TRICHLORACETALDEHYDE, $CCl_3{\cdot}CHO$. Chloral was first obtained by Liebig (Annalen, 1832, **1**, 189) by chlorination of absolute alcohol. Its composition was established by Dumas (Ann. Chim. 1834, [ii], **56**, 125) and by Städeler (Annalen, 1847, **61**, 101).

Chloral is manufactured by chlorination of absolute alcohol. Chlorination is carried out in lead or lead-lined vessels provided with a reflux condenser and a chlorine distributor taken to the bottom of the vessel, and so arranged that a maximum distribution of chlorine passes through the alcohol. The vessels, of from 400 to 1,000 gallons capacity, are about two-thirds filled with alcohol, three such vessels being arranged in series so that any excess chlorine from the first vessel passes into the second and from the second to the third in order to ensure complete absorption of the gas. The hydrogen chloride evolved during the reaction is absorbed in water. The initial reaction is vigorous and during the first stage the temperature is kept as low as possible by efficient cooling. Chlorine is passed in at a rate which results in a liquid of approximately 24°Bé. at the end of the first day's run. During the next twenty-four hours the temperature is raised gradually, heat being applied if necessary, to about 50°C., and the density of the liquid at the end of this period should be from 35°–40°Bé. The reaction is completed on the third day by increasing the temperature to 95° and continuing the chlorination until the density reaches 49°Bé. A sample of the product at this stage distilled with an equal volume of concentrated sulphuric acid should indicate a yield of about 75% of chloral. The crude chloral alcoholate is allowed to cool, when it solidifies. It is then gradually mixed with an equal volume of sulphuric acid 66°Bé, the mixture being kept cool. The temperature is then gradually raised. Hydrogen chloride is evolved, together with some ethyl chloride. Between 70° and 90° alcohol is recovered, and crude chloral passes over between 90° and 98°. The crude chloral is purified by redistillation over calcium carbonate, the portion distilling over above 94° being pure chloral.

Other processes which have been suggested include the chlorination of alcohol in the vapour phase (G.P. 133021), the chlorination of a mixture of acetaldehyde and alcohol (F.P. 612396), and the chlorination of acetal (Reichert, Bailey, and Nieuwland, J. Amer. Chem. Soc. 1923, **45**, 1552).

Chloral is a colourless, pungent liquid, b.p. 97·7°. When pure it is stable, but in the presence of traces of impurities such as sulphuric acid it polymerises with production of metachloral, a white amorphous solid. The same product is obtained by the action of aluminium chloride on chloral (G.P. 139392). Metachloral is insoluble in water, alcohol, ether and acids, but soluble in sodium carbonate solution. On distillation at 180°–185° it is reconverted into chloral (Kolbe, Annalen, 1845, **54**, 183). A water soluble polymeride is obtained by treating chloral with pyridine or an amine in the cold and then acidifying. Alcohol and water convert it into chloral alcoholate and chloral hydrate respectively. Alkalis decompose it, giving chloroform and formic acid.

Chloral Hydrate, $CCl_3{\cdot}CH(OH)_2$, is by far the most important derivative of chloral. It is prepared by the cautious addition of the requisite amount of water to chloral, overheating of the mixture being avoided. It is purified by crystallisation from benzene, chloroform or light petroleum. To obtain the hydrate in the form of cubes or plates rather more water is added than is theoretically necessary, the mixture thoroughly shaken until cold and the mass of crystals poured on to porcelain dishes and dried over sulphuric acid *in vacuo.*

Chloral hydrate occurs in colourless crystals m.p. 50°–58°, with a pungent odour and bitter taste, and is readily soluble in water, alcohol, chloroform, ether and oils.

Chloral hydrate is very largely employed in medicine as a hypnotic and is official in most pharmacopœias. It is of special value in simple nervous insomnia, delirium tremens, and certain forms of insanity. It is also a powerful deodorising and antiseptic agent. By itself, or in concentrated solution, it may be used as a vesicant. The toxic effects produced by overdoses of chloral hydrate are a fall of temperature and slow and enfeebled respiration.

Chloral Formamide, Chloralamide, $C_3H_4O_2NCl_3$, is prepared by gently heating chloral and formamide in equimolecular proportions. On cooling the melt sets to a solid mass which is recrystallised from water or 30% alcohol. It forms colourless crystals, m.p. 114°–115°. It is soluble in water (1 : 20) and very soluble in alcohol, ether and acetone. It is not decomposed by acids, but when warmed with dilute alkalis is decomposed, yielding chloroform, ammonia, and formic acid.

Chloral formamide is a somewhat slower acting hypnotic than chloral hydrate and is especially useful in the insomnia of cardiac disease, since it has not the depressant action of chloral on the heart. It is also used in combination with potassium bromide as a remedy for sea sickness.

Glucochloral, Chloralose, $C_8H_{11}O_6Cl_3$, obtained by heating chloral and glucose in equal parts on the water bath, forms crystals, m.p. 185°, is a hypnotic and sedative. An isomeric product, parachloralose, produced at the same time is devoid of hypnotic properties.

Butyl Chloral, Trichlorbutyric Aldehyde, $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$, is prepared by passing dry chlorine into aldehyde or paraldehyde at about −10° until the aldehyde is saturated. The temperature is then gradually raised to 100°, chlorine being continually passed in until chlorination is complete. The resulting liquid is diluted with water and then distilled in a current of steam, when the hydrate passes over. The hydrate is recrystallised from water and on distillation in a stream of hydrogen chloride the pure chloral is obtained (Pinner, Annalen, 1875, **179**, 26). It is a colourless oil with a characteristic odour, b.p. 164°–165°/750 mm. sp.gr 1·3956 at 20°/4°; fuming nitric acid converts it into trichlorbutyric acid. It readily combines with water forming the hydrate.

Butyl Chloral Hydrate,

$$CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH)_2,$$

is prepared by mixing butyl chloral with about one-ninth its weight of water and recrystallising the solid mass so formed from boiling water. It forms white trimetric plates with a pungent but not acrid odour and a nauseous, bitter taste. It melts at about 78° and resolidifies at about 71°. It is soluble in about 40 parts of water, very readily soluble in alcohol, ether and glycerine, less readily in chloroform and olive oil. Butyl chloral hydrate resembles chloral hydrate in its action, but is a weaker hypnotic and has a more pronounced depressant action on the heart. It is chiefly employed in combination with camphor, phenazone or gelsemium as an analgesic in cases of neuralgia and migraine.

A. J. E.

CHLORALAMIDE. Syn. for chloralformamide, $CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}CHO$ (*v.* CHLORAL).

CHLORAMIN *v.* ACTIVIN.

CHLORAMINE-T, sodium *p*-toluenesulphonchloroamide,

$$CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NClNa{\cdot}3H_2O,$$

first prepared by Chattaway (J.C.S. 1905, **87,** 151), is a white crystalline solid with a slight odour of chlorine and a bitter taste. It is soluble in about 7 parts of water, and may be obtained from *p*-toluenesulphonyl chloride, a by-product in the manufacture of saccharin, or directly from toluene by sulphonation and conversion to the sulphonyl chloride, which is then treated with ammonia to form the sulphonamide. This, by the action of bleaching powder or sodium hypochlorite, is converted into the dichloramine, which, in presence of excess of caustic soda, yields chloramine-T.

Chloramine-T contains about 25% of "available" chlorine. It was introduced by Dakin during the war as a solution for the irrigation of wounds to replace the much less stable hypochlorite solution, and is now included in the British Pharmacopœia. Aqueous solutions of the salt are comparatively stable and may be kept for some time without appreciable decomposition.

Technically chloramine-T finds employment in many directions in the textile industry as a bleaching agent and for the development of colour on the fibre, as well as in the manufacture of printing inks and the preparation of soluble starch for finishes, etc. It is also used in the brewing industry for general cleansing and sterilising purposes and as a preservative in the treatment of leather, and in glue and adhesives. It does not readily attack aluminium, brass, tin or enamel, and is therefore available for the cleansing and disinfection of vessels used in the preparation and storage of food products.

Dichloramine-T, *p*-toluenesulphondichloroamide, $CH_3{\cdot}C_6H_4{\cdot}SO_2NCl_2$, was also prepared by Chattaway (*l.c.*), and is a yellow crystalline powder, m.p. about 78°, having an odour of chlorine. Unlike chloramine-T, it liberates bromine from sodium bromide solution. On exposure to air it is gradually decomposed with loss of chlorine. It is sometimes employed in solution in oil as an antiseptic.

A. J. E.

CHLORANIL. Tetrachloro-*p*-benzophenone

CHLORAZENE. Syn. for Chloramine-T.

CHLORAZIDE, N_3Cl *v.* AZOIMIDE.

CHLORENE. (1) A green hydrocarbon of unknown structure obtained as a by-product in the preparation of fluorocyclene by heating acenaphthene with lead oxide at 350° (Dziewonski and Suknarowski, Ber. 1918, **51,** 457). Dilute solutions in benzene are pure green in colour, more concentrated solutions are purple-red; chlorene solutions undergo photochemical oxidation on exposure to light. The absorption spectrum shows three well-defined bands in the visible region.

(2) The term "chlorene" has also been applied to a yellow gaseous hydrocarbon, C_4H_4 made by passing acetylene through a quartz tube at 750°. Its reactions are similar to those of acetylene, and it is slowly converted at the ordinary temperature to a colourless isomer (Mignonac and Ditz, Compt. rend. 1934, **199,** 367).

CHLORETONE. Chlorbutol. Trichloro-*tert*-butyl alcohol, $Me_2C{\cdot}CCl_3{\cdot}OH$. Sedative.

CHLORINE.

Historical.—Chlorine must have been known, according to Mellor ("Inorganic and Theoretical Chemistry," Vol. II, p. 20), to many alchemists from the thirteenth century onwards. It is, however, to Scheele that we owe the first adequate description of the preparation in 1774 of "dephlogistigated marine acid air" obtained during his researches on the properties of black oxide of manganese.

Lavoisier and Berthollet, a few years later, preferred the name "oxymuriatic acid," and the view that it was a compound persisted until 1809, when Gay Lussac and Thenard suggested it was an element. In 1810, Davy adduced evidence which was regarded as conclusive that the gas was an element, the characteristic colour of which led him to suggest the name chlorine.

The observation of the bleaching properties of the gas and its solutions in water led Berthollet, 1785, to its practical application, and in 1789 to make the still more convenient alkaline bleaching solution. The solution of chlorine in caustic potash became known as Eau de Javelle, whilst the solution in caustic soda became Eau de Labarraque. The name Eau de Javelle is still widely used, but nowadays refers to a solution of sodium hypochlorite.

The fact that bleachers in Lancashire had used a solution of chlorine in milk of lime prevented Tennant, 1798, from obtaining a valid patent. In 1799, however, Tennant patented the use of dry hydrated lime to absorb chlorine to make "bleaching powder," and thus was born one of the major heavy chemical industries. Manufacture of bleaching powder, which was first carried out in Glasgow, spread rapidly as the alkali manufacturers realised its importance, particularly as an outlet for their waste hydrochloric acid.

The production of chlorine and caustic soda when an electric current passes through a solution of common salt was observed at the beginning of the nineteenth century. Industrial development of this process, however, waited on the supply of cheap mechanically-produced electric energy introduced with the Gramme dynamo-electric machine in 1872. Commercial development occurred with increasing intensity from that date.

Occurrence.—Chlorine, apart from volcanic gases, never occurs in nature in the free state (Shepherd, J. Washington Acad. Sci. 1920, **10,** 23). In combination with other elements it occurs as:

1. Sodium chloride in sea water and in rock salt deposits.
2. Potassium chloride alone and combined with magnesium chloride or sulphate in salt deposits.
3. The chlorides of calcium, magnesium,

lead, copper, iron, manganese, mercury and silver.

4. Hydrochloric acid in volcanic gases and springs.

5. Sodium and potassium chlorides in the vegetable and animal kingdom and as hydrochloric acid in the gastric juice.

The chief chlorine supplies are derived from salt deposits formed by the evaporation of inland seas or sections of the sea isolated by change in land levels. Solar salt produced by evaporation of sea water is used to a minor extent as a source of chlorine.

Sodium chloride in the form of rock salt occurs in large deposits in England, Germany, Austria, France, Spain, Russia, Canada and the U.S.A. Deposits occur in various geological formations: in England, for example, the rock salt is found in the Keuper marl, a Triassic formation, whilst the deposits in the States of New York and Michigan and in Ontario occur in Silurian rocks.

Potassium chloride is found associated with other salts in the Dead Sea, and is one of the products of the solar evaporation practised there. The chief sources of potassium chloride are the deposits of Stassfurt, Alsace-Lorraine and Spain, where it is found combined with other salts, as, for example, $KCl{\cdot}MgCl_2,6H_2O$, carnallite.

Laboratory Preparation.—The oldest method of preparing chlorine for laboratory purposes consists in heating manganese dioxide with hydrochloric acid:

$$MnO_2+4HCl=Cl_2+MnCl_2+2H_2O$$

The most convenient means of obtaining chlorine in the laboratory is from a cylinder of the liquid. The liquid is not, however, quite pure, containing small quantities of bromine, organic compounds, and dissolved gases, the total of such impurities being less than $\frac{1}{10}$% by weight.

When pure chlorine is required, the method of von Graebe may be used. Analytical quality hydrochloric acid is allowed to drip on to crystals of potassium permanganate covered with water, a gentle heat being supplied to give a steady evolution of the gas.

Physical Properties.—At. wt. 35·457 ; atomic no. 17 ; isotopes 35, 37.

Properties of the Gas.—Density at N.T.P. 3·214 g./litre. This density is about 1·7% greater than required by the gas laws, but very close approximation to the ideal density occurs above 300°C. Above 1,137°C. dissociation into atomic chlorine occurs to some extent (Reinganum, Physikal. Z. 1905, **6**, 1514).

The mean value of the coefficient of expansion at atmospheric pressure and ordinary temperature is 0·003836 (Jaquerod and Tourpaian, J. Chim. phys. 1913, **11**, 15).

Heat capacity at 15°C., and 1 atm. Cp= 0·115 cal./g. The ratio Cp : Cv=1·355.

The explosive limits of mixtures of hydrogen and chlorine are 91·9% Cl_2 and 8·1% H_2 to 14·3% Cl_2 and 85·7% H_2, when using an induction coil spark (P. Mathieu, J. Physique, 1917, **7**, 166).

Properties of the Liquid.—B.p. −34·6°C. The vapour pressure in atmospheres, the densities of the liquid and the saturated vapour are (D= g./ml.):

Temp. °C.	P. atm.	D. liquid.	D. vapour.
−34·6°	1·00	1·561	—
−20°	1·84	1·524	—
−10°	2·61	1·496	—
0°	3·65	1·468	0·0128
+10°	4·96	1·438	0·0175
+20°	6·57	1·408	0·0226
+30°	8·60	1·377	0·0300
+50°	14·1	1·310	0·0486
+100°	37·6	1·109	0·136

Critical temperature 144°C. Heat capacity −85·4°C. to −76·1°C.=0·229 cals./g. Surface tension 27 dynes/cm. at the boiling-point. Viscosity 0·494 centipoises at −35·4°C.

The expansion coefficient is:

t°C.	−88° to −33·6°	−33·6° to 0°
$a\times10^3$	1·409	1·793

t°C.	0° to 30°	30° to 60°	60° to 90°
$a\times10^3$	2·066	2·55	3·5

Latent heat of vaporisation at −22°C. = 67·4 g.-cal. at + 8°C.=62·7 g.-cal.

F.p. −103°C. with vapour pressure 8·9 mm.

Latent heat of fusion 1·626 kg.-cal./g. mol.

Solubility.—At total pressure 760 mm. l is the volume of gas dissolved by 1 vol. of water (gas volume reduced to N.T.P.), and q is the weight of gas in g. dissolved in 100 g. of water.

t°C.	10	11	12	13	14
l .	3·148	3·047	2·950	2·856	2·767
q .	0·9972	0·9654	0·9346	0·9050	0·8768

t°C.	15	16	17	18	19
l .	2·680	2·597	2·517	2·440	2·368
q .	0·8495	0·8232	0·7979	0·7738	0·7510

t°C.	20	25	30	40	50
l .	2·299	2·019	1·799	1·438	1·225
q .	0·7293	0·6413	0·5723	0·4590	0·3925

The heat of solution for 1 mol. in 1,000 mols. water is 4.96 kg.-cal. Chlorine is more soluble in 14% aqueous hydrochloric acid and less soluble in salt solutions than in water:

20°C. wt. % HCl	4·13	6·61	8·74	10·40	13·94
20°C. wt. % Cl_2	0·703	0·722	0·743	0·769	0·823

(Oliveri-Mandalá, Gazzetta, 1920, **50**, 94).

In saturated $NaCl$ solution:

t°C. . . .	14·5°	29·0°	60·0°
Wt. % Cl_2 .	0·0966	0·0842	0·0364

Chlorine is also readily soluble in inorganic liquids, such as $SiCl_4$, $SnCl_4$, SO_2Cl_2, and CrO_2Cl_2, etc.

At 0°C. $SiCl_4$ dissolves 13% Cl_2 by weight.

At 0°C. SO_2Cl_2 dissolves 14% Cl_2 by weight.

Organic liquids also dissolve chlorine:

CCl_4	t°C. .	0	19	40
	Wt. % Cl_2.	15·6	8·48	4·33
$CHCl_3$	t°C. .	0	10	
	Wt. % Cl_2.	22·0	20·0	—

Acetic acid at 15°C. :

Wt. % Acetic acid	99·84	90·0	75·0	65·0
Wt. % Cl_2 . .	10·6	7·14	4·65	3·81

Chlorine Hydrate.—On cooling a solution in water saturated with chlorine at atmospheric pressure below 9·6°C., yellow crystals are deposited. Moist gas on cooling below 9·6°C. also deposits the same substance, which is a hydrate of chlorine. The hydrate formed under different conditions of temperature, pressure and relative concentration of the constituents, has the composition $Cl_2,6H_2O$ (Anwar-Ullah, J.C.S. 1932, 1176.

The hydrolysis of chlorine in water was studied by Jakowkin (1899), who found equilibrium was attained at 25°C. after 48 hours. Increase in temperature favours the hydrolysis and decreases the time required to reach equilibrium (Z. physikal. Chem. 1899, **29**, 613).

The photolysis of chlorine in water (Allmand, Cunliffe and Maddison, J.C.S. 1925, **127**, 822; 1927, 655) has been investigated, and an explanation given for the mechanism of the reactions which produce hydrochloric and chloric acids together with oxygen.

For more complete physical data see " Comprehensive Treatise of Inorganic Chemistry," Vol. II, by J. W. Mellor; " International Critical Tables " ; Gmelin's " Handbuch der anorganischen Chemie. System No 6." Landolt-Boernstein, Tabellen.

Chemical Properties.—Chlorine is a very reactive substance, and even a small percentage of the gas in air has a characteristic pungent and irritating smell; the danger of breathing chlorine is not that it is a true poison, but that it rapidly attacks the mucous and lung membranes, causing congestion.

Chlorine combines with most elements with con. siderable evolution of heat and in some cases with ignition, when uncontrolled reaction takes place.

Phosphorus ignites spontaneously in the gas, forming phosphorus trichloride. Finely-divided arsenic, antimony, copper, tin, lead and iron burn in chlorine, forming the respective chlorides, but most of these metals, when in bulk, behave quite differently. The action of chlorine on metals is also profoundly affected by the amount of water present, the amount of reaction decreasing with decreasing water content. The indifference of dry chlorine to steel enables liquid chlorine to be manufactured and shipped in steel vessels.

Chlorine and hydrogen may be mixed together in the dark without combining, but such mixtures explode violently in bright daylight or when heated.

Either alone or in the presence of catalysts, chlorine combines with many inorganic chemical compounds, *e.g.* sulphur dioxide, carbon monoxide, phosphorus trichloride, ferrous chloride, stannous chloride.

With olefins, acetylenes, and benzene (under certain conditions) chlorine combines directly, forming additive compounds. The uncontrolled reaction with acetylene is explosive. With turpentine, the reaction is so violent that the oil inflames with production of carbon and hydrogen chloride.

With saturated organic compounds, chlorine forms substitution products and the eliminated hydrogen is simultaneously converted into hydrogen chloride. With benzene and other aromatic organic compounds, addition or substitution products or both are formed according to the temperature, and catalyst conditions.

LIQUID CHLORINE.—Liquid chlorine was first obtained in 1805, by Northmore. The pure gas can be condensed to a liquid at 15°C. by a pressure of about 6 atmospheres, or at atmospheric pressure by reducing its temperature to −35°C. Chlorine gas from electrolytic cells varies in strength from 90% upwards ; the impurities consist of air, drawn in by working the cells under slight suction, carbon dioxide, and oxygen from hydroxyl, sulphate and chlorate ion discharge, and hydrogen from the cathode. The impure gas obviously requires a higher pressure or lower temperature than the pure gas for liquefaction and some chlorine must be carried over by the contaminating gases and lost. Moreover, a limit is set to the extent of liquefaction by the hydrogen content of the residual gas, which for safe working must not reach the explosive limit.

Liquid chlorine was first produced commercially by Knietsch for the Badische Anilin und Soda Fabrik in 1888 (B.P. 13070, 1888). The liquefaction was accomplished by compression with condensation at ordinary temperatures. The compressor was of the liquid piston type using concentrated sulphuric acid to confine and compress the chlorine gas; the sulphuric acid was in turn moved by a liquid piston of paraffin oil. The adoption of such a complicated apparatus is some measure of the difficulties met in attempting to provide commercial liquid chlorine. Although steel is relatively unaffected by dry chlorine at ordinary temperatures, at higher temperatures the rate of reaction increases and becomes very appreciable at 130°C. This strictly limits the compression ratio that can be used. Moreover, lubrication is difficult, since all the usual lubricants are attacked by chlorine. Sulphuric acid appears to be the favourite choice as a lubricant.

At present liquid chlorine is produced by (i) compression with condensation at ordinary temperatures, (ii) refrigeration alone, or (iii) a combination of compression and refrigeration.

Transport.—The transport of liquid chlorine is governed by the rules and regulations of railway companies and of authorities such as the Board of Trade for shipments by sea.

Regulations in the United States (and by voluntary concurrence in Canada) are issued by the Inter-State Commerce Commission to which the Chlorine Institute (an association of producers) acts in an advisory capacity.

In Great Britain advisory bodies appointed by the Home Office have published two relevant reports—the Fourth Report of the Gas Cylinders Research Committee (Cylinders for Liquefiable Gases), 1929, H.M.S.O., and the Welded Containers Report, 1931, H.M.S.O. A summary of the various national regulations and of British practice in " The Handling and Use of Liquid Chlorine " has been given by F. Holt (J.S.C.I. 1936, **55**, 245–255, 269–272).

Liquid chlorine is supplied in three different types of container:

(*a*) Cylinders varying in capacity to 150 lb.

	England.	U.S.A.	Germany.
(*b*) Drums, capacity	1,900 lb.	2,000 lb.	1,000 kilos.
(*c*) Tank wagons, capacity	14 tons	16 and 30 short tons	14 tonnes

In charging liquefied gas containers special precautions must be taken to ensure that ample " free space " is left so that the container cannot become completely filled with liquid with consequent risk of extremely high hydraulic pressure. The British filling ratios of 1·25 and 1·19 lb. of chlorine per lb. of water capacity for temperate and tropical conditions respectively are based on 6% free space at 45°C. and 65°C. These ratios are for solid drawn cylinders; for welded containers the British filling ratios are 1·24 and 1·16 based on 6% free space at 50°C. and 75°C. respectively.

Containers should be stored in a cool, dry place, preferably fireproof. Care should be taken in the handling of containers; the strength of the containers should not be abused by exposing them to falls. If a container is allowed to remain coupled to an absorption plant after all the liquid chlorine has evaporated, the residual chlorine in the pipe-line and container will dissolve, causing the liquid in the absorption vessel to be drawn back into the container. This might have serious results, owing to the decomposition of some of the liquids under certain conditions causing a burst.

Applications.—The largest consumption of liquid chlorine takes place in the paper industry, where it is used both for the preparation and bleaching of pulp.

In the textile industry it is used in the bleaching of cotton and viscose and in the production of unshrinkable woollen goods. When used for bleaching it may be absorbed in caustic alkali to make the corresponding hypochlorite, or it may be absorbed in sodium carbonate solution to make hypochlorous acid:

$$\mathrm{Na_2CO_3+Cl_2+H_2O = HOCl+NaHCO_3+NaCl}$$

This acts approximately twice as energetically as the corresponding amount of neutral hypochlorite.

It is used in the manufacture of chlorinated organic products, such as carbon tetrachloride, trichlorethylene, chloroform, monochloracetic acid, and derived products like ethylene glycol and ethylene oxide; for the chlorination of methane to methyl chloride and methylene chloride, and for the chlorination of benzene, toluene, naphthalene and diphenyl.

Chlorine is used for the preparation of the chlorides of aluminium, boron, titanium, sulphur, antimony, iron and tin, and for degassing molten aluminium prior to casting. Formerly considerable quantities of tin were recovered as tin tetrachloride in the Goldschmidt process for detinning of scrap. The process is still in use, but is of less importance for tin recovery as the percentage of tin on tin scrap has steadily fallen from 2% to less than 1%. The residual iron is recovered by smelting.

Phosgene is made by the combination of carbon monoxide and chlorine, and sulphuryl chloride by combination of sulphur dioxide and chlorine.

Many of the above uses of chlorine have been developed because of the necessity of finding new outlets for the enormous quantities of chlorine produced in recent years by the electrolytic processes for preparing caustic potash and caustic soda.

Certain organic chlorine compounds having lachrymatory, sternutatory, and other toxic properties were used in the Great War (J.S.C.I. 1918, **37**, 127 R, and Tone, Chem. Met. Eng. 1918, **19**, 357) (*v.* CHEMICAL WARFARE).

TREATMENT OF WATER.—The complete sterilisation of potable water and complete or partial sterilisation of industrial waters such as condenser water for power stations, water for swimming baths, trade effluents from works (discharging fermentable matter) and sewage, has become a most important matter for the general well-being of the community.

The importance of sterile water for domestic purposes has long been realised, and the incidence of water-borne disease may be said to be completely within control since the adoption in one form or other of the application of chlorine in small regulated quantity.

Chlorine treatment is also applied to sterilise water for swimming baths, to condenser water in order to prevent the growth of low forms of life in gelatinous form which prevents efficient transfer of heat, and to sewage and fermentable trade wastes in order to prevent undesirable anaerobic fermentation and to assist in the control of aerobic fermentation.

There are three general methods in use, all of which involve the use of instruments to provide measured quantities of chlorine. These methods are (1) chlorine treatment, (2) chloramine treatment, (3) hypochlorous acid treatment.

In water or sewage, etc., to which chlorine, chloramine, or hypochlorous acid has been added, the chlorine will occur in various forms, such as free chlorine atoms and molecules in solution, as $\mathrm{OCl'}$ ions and as HOCl molecules, as well as in the form of various compounds with organic matter, etc., such as chloramines, and possibly also loose addition compounds. Most of these are known to have powerful germicidal properties, and the following suggestions have been put forward in explanation:

(1) That sterilisation is due to direct chlorination of the cell protein.

(2) That sterilisation is due to oxidation of the cell material, the oxygen being formed by the action of the chlorine and/or chlorine compounds on water.

There is a certain amount of evidence in support of each of these hypotheses, and it seems quite possible that at times both may be important factors.

That chlorine does act as a chlorinating agent is known by the fact that the objectionable taste of certain waters containing organic matter may be surmounted by over-chlorination followed by dechlorination with sulphites, etc., or by the chloramine process.

Water when treated with ammonia prior to its treatment with chlorine is found to have the advantage that objectionable tastes do not develop, whilst the sterilisation is just as good as with chlorine only. It is claimed for this process that the water is delivered sterile to the consumer owing to the greater stability of chloramine in solution.

The chlorine and chloramine treatments are used largely in Britain and U.S.A., whereas the hypochlorous acid treatment is of growing importance in Germany, where it has been successfully used for many years. It is claimed for the hypochlorous acid process that it has been particularly successful in many cases where neither chlorine nor chloramine treatments were entirely effective and that in other cases it has given equally good results.

The hypochlorous acid for this treatment is produced in stoneware towers, where a measured quantity of chlorine is passed counter- or co-current to (1) a measured quantity of sodium carbonate solution (G.P. 306193, 1916, Deutsche Solvay-Werke A.-G.); (2) water passing over marble (G.P. 632713, 1932; B.P. 412105, 1933, Ornstein); (3) water passing over moulded magnesia (G.P.*a.* 72332, 1936, Deutsche Solvay-Werke A.-G.). *See also* "The Examination of Waters and Water Supplies," by J. C. Thresh, J. F. Beale, and E. V. Suckling, published by J. and A. Churchill, London.

Production of Chlorine.

Introduction.—All manufacturing processes for chlorine involve the balancing of demands for chlorine and at least one other product.

With processes starting from hydrochloric acid, the other primary product is saltcake, (Na_2SO_4), which was an intermediate in the production of sodium sulphide, soda ash, and caustic soda by the Leblanc process.

For many years the production of chlorine from by-product hydrochloric acid enabled the Leblanc process to compete with the ammonia-soda process, but the introduction of direct electrolytic preparation of caustic soda and chlorine gave the same end products and eventually displaced the Leblanc process by reason of lower costs.

In recent times special conditions have been examined and two interesting proposals have been made.

(1) The first deals with the situation where there is a large local demand for sodium sulphate or sodium sulphide with no outlet for hydrochloric acid. In this case electrolysis of hydrochloric acid to give hydrogen and chlorine has been proposed.

Westvaco Chlorine Products Inc. and F. S. Low have described (B.P. 348792) a diaphragm cell for the electrolysis of hydrochloric acid. Copper is preferred as a cathode, but nickel or monel metal may be used. The cathode is surrounded by a diaphragm of acid-resistant asbestos cloth. The anode is graphite.

The hydrochloric acid solution enters the cathode compartment, passes through the diaphragm, and leaves the cell by way of the anode compartment. The weak acid is dechlorinated by air blowing and is then resaturated, heated, and recirculated.

The inlet and exit acid strengths are 20% and 10% respectively. Preferred temperatures are 45°-100°C., and voltages as low as 2·1 are claimed. It is stated that the chlorine is of 99·9% purity and that carbon dioxide and oxygen are absent.

(2) The second proposal arises from the fact that caustic soda produced by electrolysis must displace caustic soda otherwise produced by causticising soda ash. The demand for chlorine has resulted in America in a large over-production of caustic soda and efforts have been directed to working out economical alternative processes for the production of chlorine. Coupled with the above situation the market price of sodium nitrate has fallen so low that it is very much less profitable than formerly to manufacture sodium nitrate from soda ash and synthetic nitric acid.

It has therefore been suggested that sodium nitrate and chlorine might be more profitably manufactured by the action of nitric acid on sodium chloride. F. W. de Jahn (Chem. Met. Eng. 1935, **42**, 537).

In addition to the primary reactions,

$$NaCl + HNO_3 = NaNO_3 + HCl,$$
$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O,$$

the $NOCl$ reacts with water and air regenerating HNO_3 and HCl, the regenerated HCl reacts again with the HNO_3, so that the net result is the oxidation of the HCl by the oxygen in the air with recovery of the HNO_3.

It is interesting to note that the similar Dunlop process was employed at St. Rollox Works, Glasgow, about 1850. Here the nitrosyl chloride was decomposed by sulphuric acid, the consumption of which was, however, so large that the process was abandoned.

It is evident that the discovery of suitable resistant materials of construction will play an important part in the working of this process.

HISTORICAL.

1. *The Older Processes*: *Oxidation.*—Chlorine was first produced on a reasonably large scale for Javelle water and for bleaching powder by oxidation of hydrochloric acid made by treating salt with sulphuric acid, by naturally occurring manganese dioxide—pyrolusite:

$$2NaCl + 2H_2SO_4 + MnO_2$$
$$\rightarrow Na_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$$

The development of the Le Blanc process for alkali gave rise to large volumes of hydrogen chloride, which were at first discharged *via* a chimney stack to atmosphere. The patent of Gossage (1836) showed how the nuisance so created could be abated by washing out the acid gas in a coke-packed tower in a counter-current stream of water. The hydrochloric acid so obtained was immediately applied to the production of chlorine by reaction with manganese dioxide:

$$4HCl+MnO_2 \rightarrow MnCl_2+Cl_2+2H_2O$$

The by-product hydrochloric acid, of little value otherwise, gave a much cheaper chlorine than the previous process. Nevertheless, the imported manganese ore was expensive and the process was wasteful of this raw material. Weldon (1866) developed a successful recovery process which conserved manganese with great economy. The liquor from the chlorine stills, containing manganese chloride, excess acid, iron chloride and other impurities, was carefully neutralised with ground limestone, and precipitated hydroxide of iron was allowed to settle out. The clear liquor was treated with about a 20% to 30% excess of milk of lime to precipitate the manganese as hydroxide. Steam heating was applied and the manganous hydroxide was oxidised by air blowing, the final product being a calcium manganite,

$$CaO{\cdot}2MnO_2.$$

The precipitate known as " Weldon mud " was recovered and returned to the chlorine stills.

The Weldon process, though more economical of manganese, still only showed about a 30% conversion of hydrogen chloride to chlorine, the remainder being lost as calcium chloride.

Deacon (1868) evolved a successful method of air oxidation of hydrochloric acid using copper chloride as a catalyst. Although this process gave a much better yield on the hydrochloric acid and prior condensation of hydrochloric acid was avoided, there were many difficulties, chief of which was the poisoning of the catalyst by arsenic and sulphur compounds. The product of the reaction after removal of excess hydrochloric acid and steam by condensation was chlorine diluted with nitrogen from the air.

The process of Hasenclever (1883) for obtaining reasonably pure hydrogen chloride by dehydrating the aqueous acid with oil of vitriol which could subsequently be reconcentrated was of benefit to the Deacon process, and rapid headway was made.

The Deacon process depends essentially on the equilibrium

$$4HCl+O_2 \rightleftharpoons 2Cl_2+2H_2O,$$

although it is presumed that the catalyst functions by decomposition of cupric chloride to chlorine and cuprous chloride, cuprous chloride is oxidised to copper oxychloride, and this in turn is converted by HCl into cupric chloride, the cycle being repeated.

2. *The Modern Processes*: *Electrolysis*.—The patent of Watt (B.P. 13755, 1851) covered a very wide range of electrolytic processes, including the electrolysis of brine to give chlorine and caustic soda. Cooke (B.P. 13620, 1851) described a cell for carrying out the method, and Stanley (B.P. 811, 1853) also described a process.

The high cost of electric energy at that time, however, ruled out these as industrial enterprises.

The difficulties experienced in the electrolytic decomposition of alkali chlorides on a manufacturing scale have been first the cost of the electric current, which was absolutely prohibitive until the dynamo-electrical machine had been so far developed as to be a commercial reality, viz. in 1872 by Gramme. When it became possible to conduct electrolytic experiments on the large scale over long periods of time, it was soon found that there were many and serious difficulties, as the corrosion of the anodes, the evolution of gas from the cathode, the rapid disintegration of the diaphragms, which were either excessively porous or not sufficiently porous. There were also excessive resistances, voltages, and the generation of heat, and there were secondary reactions, so that neither the chlorine nor the alkali metal product was obtained in the expected purity or quantity.

The various electrical processes suggested or tried for the decomposition of alkali chlorides are all attempts to overcome economically these difficulties. Workers in this field, such as Fitzgerald and Motley (1872), Wastchuk and Gloushoff (1879), and others continued to patent processes.

An industrial electrolytic alkali-chlorine process may be said to date from the work of Matthes and Weber (D.R.P. 34888, 1885), who discovered a satisfactory diaphragm by means of which separation of anolyte and catholyte could be achieved. The diaphragm was made from Portland cement and salt, the latter after removal in solution giving the desired porosity. This achievement was developed by Chemische Fabrik Griesheim, later Griesheim-Elektron, and the first large-scale plant taking 400 H.P. was operated in 1890.

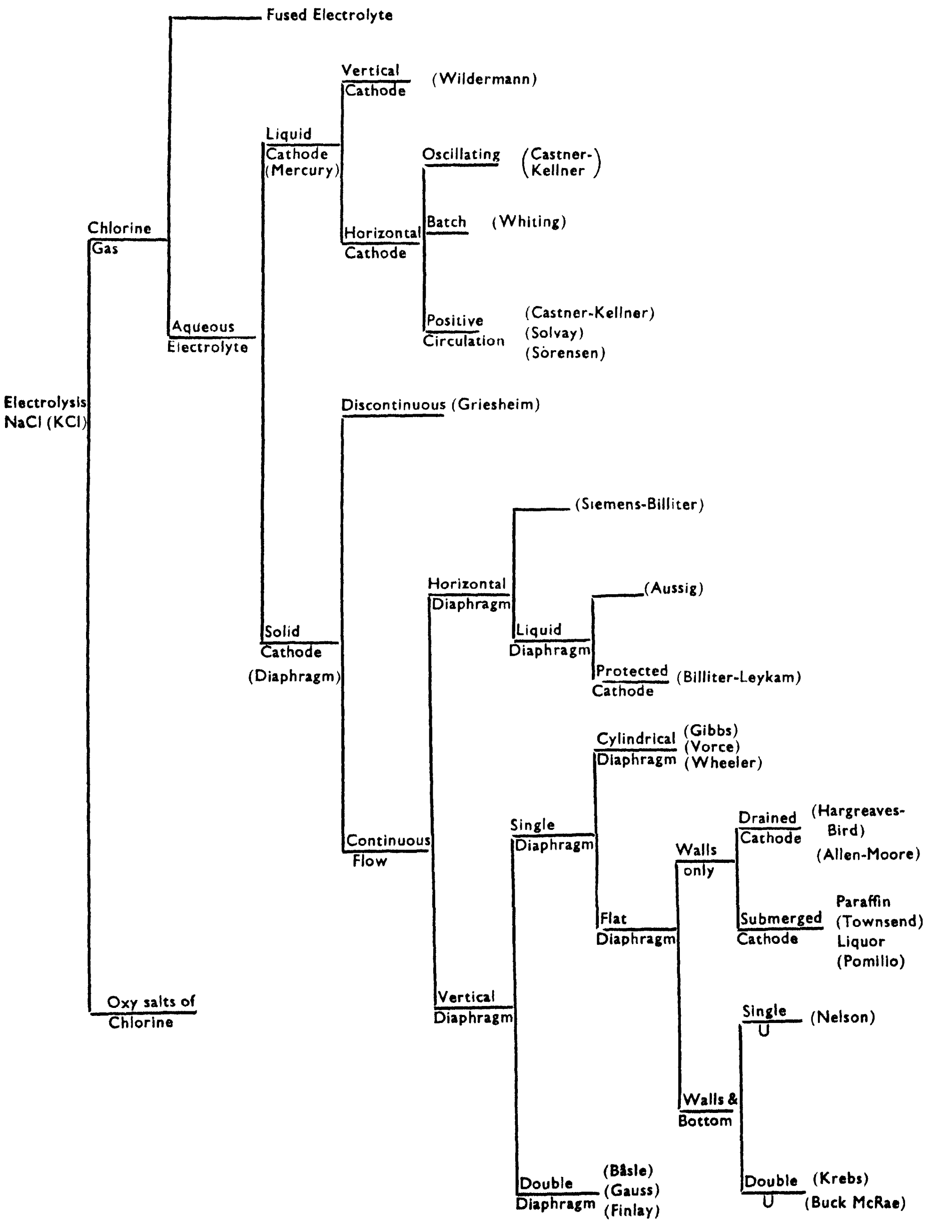
About 1890 numerous different types of cell were patented, of which that of Le Sueur (B.P. 5983, 1891), which was operated in the Eastern States of America, should be noted as the first horizontal diaphragm cell. Carmichael's cell (U.S.P. 518710 and 637851) was also developed in the same area.

These cells, like that of Griesheim-Elektron, were discontinuously operated diaphragm cells with submerged cathode. The cathode chamber was filled at the beginning of each cycle with water or dilute caustic soda which gradually increased in strength. Diffusion of sodium chloride from the anode chamber which necessarily took place and contamination with sodium hypochlorite and chlorate necessitated after a time cessation of electrolysis, removal of the catholyte and recommencement of the process after addition of fresh liquor.

The Hargreaves-Bird cell (B.P. 18871, 1892, and others) introduced a new principle in the non-submerged cathode. The cathode in this case, made of perforated steel sheet or iron wire mesh, was in close contact with the diaphragm, and the cathode liquor trickled down the cathode and the diaphragm wall to a sump.

To reduce the tendency for hydroxyl ion to diffuse back to the anolyte, carbon dioxide was admitted to the cathode chamber and sodium carbonate was produced. Steam was also admitted with the carbon dioxide to assist in heating the cell. This process was operated until 1928 by Electro-Bleach and By-Products, Ltd., at Middlewich, Cheshire, and small units

Diagram showing Classification of Chlorine Cells according to Type



were erected at cellulose factories in Austria and U.S.A. This type of cell, omitting the use of carbon dioxide, is the forerunner of three cells, viz.: Allen-Moore, Gibbs and Nelson, which, with numerous slight variants, represent the most frequently employed diaphragm cells at the present time.

The development of a horizontal diaphragm in the well-known Siemens-Billiter cell took place in 1907 about the same time as the more modern vertical diaphragm cells were evolved.

An attempt to dispense with diaphragms completely gave rise to the bell-jar or specific gravity cell, which was investigated by Richardson and Holland at St. Helens in the 'nineties (B.P. 2297, 1890). The only industrially successful cell of this type was that of Verein für Chemische und Metallurgische Produktion (D.R.P. 141187, 1900) installed at Aussig (Czechoslovakia).

The mercury cell was devised almost simultaneously by Castner (B.P. 16046, 1892) and Kellner (D.R.P. 70007, 1892), and others. This process, which was working industrially in 1895, has been developed from that date chiefly by the Castner-Kellner Alkali Co., Ltd., in England, the Castner Electrolytic Co. (later Mathieson Alkali Works) in U.S.A., and by Solvay & Co. in Europe.

In more recent times attention has been directed to the electrolysis of fused sodium chloride to give sodium and chlorine, *see* Danneel and Stockem (Z. Elektrochem. 1905, **11**, 209); Danneel, *ibid.* 1924 **30**; Gesellschaft für Chemische Industrie in Basle (The Ciba Cell); (G.P. 236804, 1909; B.P. 18300, 1910; 17047, 1911); Roessler and Hasslacher Co. (The Downs Cell), (B.P. 238956, 1924).

The Ciba cell is worked at Monthey, and the Downs cell is worked by the Roessler and Hasslacher Chemical Co. in America, and by Deutsche Gold- und Silber-Scheideanstalt, in Germany.

Further reference should be made to "Monographien über angewandte Elektrochemie," W. Knapp, Halle 1933 (vols. 23, 41, 33); Chem. Trade Journal, 1924, Elliott, "Electrolytic Caustic Soda"; J.S.C.I. 1924, **43**, 1224, 1250, 1291, Hale, "Modern Electrolytic Cells"; Chemical Markets, **30**, 147, "U.S.A. Chlorine Supplies"; Mantell, Performance and Characteristics of Electrolytic Cells, (Chem. Met. Eng. 1931, **38**, 88).

The effective development of aqueous electrolytic chlorine processes thus occurred between 1890 and 1900, and from the beginning of the century this was an established industry, rapidly expanding at the expense of the Le Blanc process which died out by 1920. The industry is still growing owing to the increasing demands for chlorine products and the discovery of new uses.

The number of types of cell in operation is quite large, as will be seen in the diagram on p. 42, which, although not complete, includes the important cells in the different classifications to which they belong, as well as some that have ceased to be used. The cells will be described under the broad classifications of diaphragm and mercury cells.

Production of Chlorine by Oxidation of Hydrochloric Acid.

(*a*) MANGANESE DIOXIDE.—*Technical.* There is divergence of opinion as to the course of the reaction between manganese dioxide and hydrochloric acid.

The first reaction is either

$$MnO_2+4HCl=MnCl_4+2H_2O,$$

or more probably,

$$2MnO_2+8HCl=Mn_2Cl_6+4H_2O+Cl_2$$

(*cf.* W. W. Fischer, Chem. News, 1878, **37**, 250; U. S. Pickering, *ibid.* 1879, **39**, 225; Berthelot, Compt. rend. 1880, **91**, 251).

The chlorides $MnCl_4$ and Mn_2Cl_6 form dark brown solutions which quickly decompose even at ordinary temperatures, and the ultimate result is

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2;$$

but this reaction is only completed at 100°C., and with a certain excess of HCl—in practice at least 10% and more if low strength acid and hard manganese ore are used—even to twice the theoretical requirement.

The manganese chloride liquor from the stills also contains free acid, the chlorides of other metals present in the ore, and a little chlorine.

Black's analysis of still liquor in a well-conducted works showed how incompletely the acid is utilised.

$MnCl_2$	10·6
HCl	6·6
Al_2Cl_6	0·6
Fe_2Cl_6	0·5
Cl_2	not determined.
H_2O (by diff.)	81·7
	100·0

On the assumption that all the manganese in the ore was in the form of MnO_2, and that no hydrochloric acid gas was carried away by the chlorine, it follows that out of every 100 parts of HCl added 33·6 parts had been left untouched.

The original source of manganese was invariably pyrolusite, which occurs in quantity in Germany, Bohemia, Transylvania, Russia, India, Australia, Japan, U.S.A., and scantily in North Wales.

A good pyrolusite should contain most of the manganese as dioxide, since the lower oxides are less useful.

Russian pyrolusite varies between 75% and 85% MnO_2, and averages 80% MnO_2, 1% MnO, 3% H_2O.

Impurities such as $BaSO_4$ and SiO_2 are objectionable as they coat particles of the ore and prevent reaction with the acid. Carbonates waste acid and add carbon dioxide to the chlorine, rendering the chlorine less suitable for making bleach. Soft pyrolusite is more easily attacked by the acid than hard pyrolusite, and is therefore preferred.

Chlorine Generation.—For a small production of chlorine, the generating vessel or still may be made of stoneware. Fig. 1 shows one of the best forms of stoneware still intended to be heated by a water or steam bath.

The manganese ore is placed in a perforated cylinder, capacity about 1 cwt., and this is put in and taken out of the still with special tongs through the large opening. The small pipes serve as acid inlet and gas outlet respectively. The still liquor at the end of the operation is siphoned out or run off through a discharge pipe passing through the steam jacket. These small stills permit of careful and economical working so far as materials are concerned, since the acid is not diluted by condensed steam.

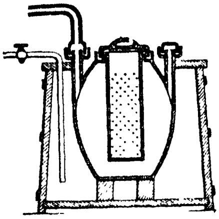


FIG. 1.

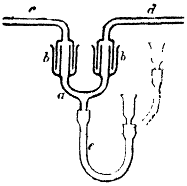


FIG. 2.

Fig. 2 shows a U-shaped pipe of lead or earthenware which permits of sealing a still of a battery from the chlorine main by means of a water seal—a most practical device.

For generating large quantities of chlorine the stills are made of highly silicious sandstone or other stone not acted upon by acids, impervious to them and not liable to crack by rapid changes of temperature. Such stone, found at Southowram, is known as "Yorkshire flag." A small, old-fashioned stone still is shown in Fig. 3, which represents it cut through the middle. These stills measured inside 7 ft. by 5 ft. by 3 ft. and upwards.

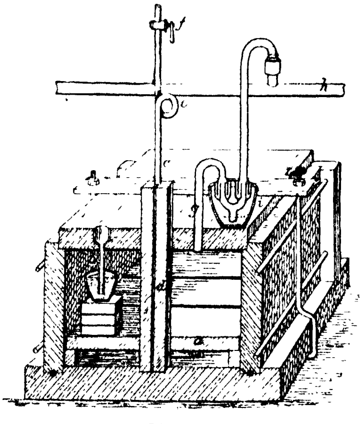


FIG. 3.

(*a*) False bottom.
(*b*) Hydrochloric acid inlet sealed in a bowl.
(*c*) Lead steam pipe connected to .
(*d*) Stoneware steam column perforated above the bottom slab.
(*g*) Chlorine outlet.

Charging opening not shown.

The small stills were worked by first adding the acid, then inserting the perforated ore container ready charged and rapidly making the joints as the reaction begins forthwith. When it slackens heat is gradually applied until the acid is exhausted. The still cools down overnight, the perforated container is removed and washed, and after removal of the still liquor the cycle is recommenced.

The large stone stills are charged with 6 to 10 cwts. of ore broken into pieces, the manhole closed and acid run in at first quickly and then gradually over several hours. The heat of reaction assists the evolution of chlorine, and when this slows down steam is injected cautiously, the temperature rising to 90°C. In the early days of the process the waste liquor evolving chlorine caused considerable nuisance and it became necessary to run it into closed vessels to which chalk or limestone dust was added, and this was subsequently the first stage of the Weldon process.

The chlorine evolved is always contaminated with HCl gas and water vapour, and these are removed by air or water cooling of a long string of earthenware or lead pipes in which the condensation of aqueous hydrochloric acid takes place and is drained away by trapped escape pipes.

Recovery of Manganese and Method of Utilisation.—The foundations of this process were laid in 1837 by Gossage, who precipitated the manganese with lime, ran off the supernatant liquor, and agitated the precipitate with air; oxidation was, however, very slow, and was never even half complete. In 1866 Walter Weldon made his first attempts and by 1869 his new process was in commercial use at the works of Messrs. Gamble & Co., St. Helens, and by 1871–73 had been so improved as to be adopted by all British and Continental alkali works.

The apparatus employed has received few modifications, but the conduct of the process which in the critical part is complicated and still not thoroughly explained has been more modified. In the following the plant, Fig. 4, and process are described.

The process is commenced in the stone still E. The only changes demanded by the Weldon process are: (1) that the acid employed should be as free as possible from sulphuric acid, since $\mathrm{CaSO_4,2H_2O}$, subsequently formed, entails extra expense in filter pressing; (2) that the run-off pipe for the still liquor should lead into a mud still D, which is shown in section in Fig. 4.

The neutralising wells G, G are sunk in the ground on a bed of puddled clay, and after being built are surrounded by puddled clay to prevent possibility of leakage; they are built of large stone slabs of acid-proof Yorkshire flag. On the top of the wells two large timber beams are seen supporting the wooden gate agitators. The liquor, while continuously agitated, is slowly treated with crushed chalk or powdered limestone, which is preferably very finely ground. The free HCl is first acted upon, yielding calcium chloride, which is an essential

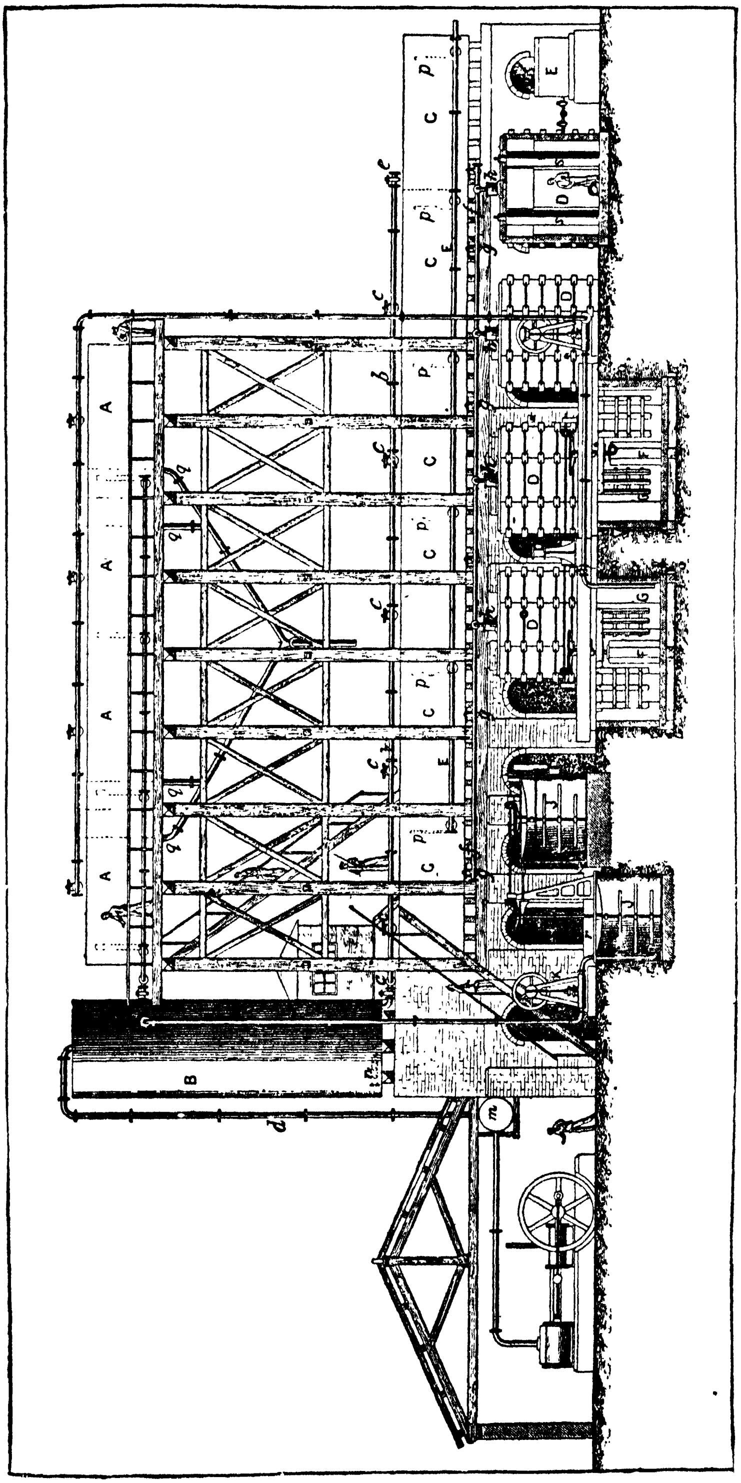


FIG. 4.

component for the remaining processes, and carbonic acid gas, which in escaping carries away the small quantity of dissolved chlorine gas ; these two objectionable gases are prevented from escaping freely into the air by covering the wells with strong planks well tarred and by leading the gases to the suction of the nearest chimney by an earthenware pipe. When the free acid has been neutralised yielding calcium chloride and Fe and Al chlorides are converted into the respective hydroxides, these last carry down as arsenites any arsenious acid originally present in the hydrochloric acid. Any sulphuric acid present in the hydrochloric acid is converted into $CaSO_4,2H_2O$. Complete neutralisation is necessary to remove the impurities and to prevent corrosion of the settling tanks A, A into which the liquor is next pumped, but the excess of $CaCO_3$ employed should be the smallest possible to reduce the cost of the subsequent operations.

A swivel pipe is lowered from above into the liquid, as shown in Fig. 4, in the left-hand well, and the turbid liquor is then piped to the gunmetal pump shown in the figure in front of the third tank D from the left. The figure shows the delivery pipe rising to the top of the plant, then running horizontally and discharging through control cocks into one or other of the four chloride of manganese settlers A, A, A, A. As soon as the well G is emptied and the pump stopped, a small valve is opened at the base of the pump delivery pipe, the pipes drained back into the well, and the swivel pipe is withdrawn, to prevent corrosion. The well is then ready to receive its next charge.

The chloride of manganese settlers are made of ⅜-in. thick boiler plates. The processes already described must be repeated until at least one settling tank A is quite full. After making the last addition the liquid should settle quite clear within a few hours, otherwise the charge in the next operation is apt to froth over, and also the recovered manganese will consume an undue amount of acid.

After the volume of the liquor in the settler A has been estimated and a sample taken for analysis, the clear liquor may be drawn off from the settler by lowering a swivel pipe just under the surface of the liquor, which can be seen to be, quite clear. The bottom end of the swivel pipe is attached to the side of the tank about a foot above the bottom of the tank so as to leave plenty of room for the mud to collect and to be stored pending its removal. Outside the tank the flow of the clear liquor is controlled by a cock, and cocks control its entrance into the oxidising tower B.

The oxidising towers B are made of ⅜-in. thick boiler plates, and they may be 8 ft. diameter and 28 ft. high, the bottom is flat, and the top is quite open. The pipe bringing the manganese chloride liquor enters the tower about 6 ft. from the top of the tower and the top of the swivel pipe may be set to give exactly the desired amount of liquor. When the liquor ceases to run the cocks are closed, and the residual liquor in the settler is reserved for the finishing of the charge.

The manganese chloride liquor should be analysed for $MnCl_2$ by diluting a measured sample with boiling water, adding zinc oxide until the mixture is white as milk, and, lastly, adding standard potassium permanganate with occasional boilings, until the supernatant clear liquor shows a pink flush ; the reaction yields a manganite exactly like the Weldon process under consideration :

$$ZnO+MnO+O=ZnO{\cdot}MnO_2;$$

and the necessary oxygen is obtained from the permanganate similarly :

$$3ZnO+2KMnO_4 \\ =K_2O{\cdot}ZnO+2(ZnO{\cdot}MnO_2)+3O$$

The temperature of the manganese liquor in the tower will be above atmospheric temperature, and in subsequent operations will be still higher, but experience has shown that if it is below 55°C. it should be heated to this point by blowing in steam. The steam pipe is not shown in the figure, and because of the shaking of the tower it must pass over the top of the tower, and terminate at the bottom of the tower in several branches containing perforations.

The manganese chloride liquor during the above heating may be agitated, and for the subsequent operation must be well agitated. This agitation is effected by a blast of air. When used for agitating purposes alone the blast of air required is not great, but the blast can be regulated as desired, and can be increased very considerably.

Milk of lime is prepared in the upper of the two tanks J, J shown in Fig. 4. Each of these tanks is provided with an agitator. The upper tank only contains a lime cage, the bottom of which is indicated by a horizontal line above the third agitator blade. This tank is filled with water, while steam is also blown in, until the hot water stands well above the level of the bottom of the cage. Quicklime is selected so as to contain less than 1% of magnesia ; it should be well burnt, but not over-burnt. The magnesia is very objectionable, because it accumulates during the repetition of the following processes, and in the generation of the chlorine it neutralises acid to no purpose. The selected quicklime in the form of large lumps is put into the cage, it soon slakes, generating thereby much heat, and this addition is continued until the milk registers 50° on Twaddell's hydrometer, the test jar being gently rotated the while ; the milk then contains 20 lb. CaO per cu. ft., and is as strong as can be conveniently prepared. The milk is then run from a valve at the bottom of the tank on to a wire sieve (not shown in the figure), and thence into the bottom tank J, which is used as a combined store and measuring tank.

The next operation is the addition of milk of lime to the hot agitated manganese calcium chloride liquor in B. It is possible to calculate the amount of milk of lime required to (1) theoretically precipitate all the $MnCl_2$, and (2) increase the total amount to 1·6 times the theoretical. Long experience with the process and due appreciation of opposing considerations have shown that this figure gives the best results for ensuring the rapidity and completeness of the oxidation, the economy of lime and of hydrochloric acid, the settling quality of the recovered manganese, and the avoidance of "stiff batches."

The milk of lime is pumped into the tower B by the pipes shown. During this operation the utmost vigilance is required in testing, samples being drawn, filtered, and tested as rapidly as possible. The first test is simply that for alkalinity with red litmus paper. A second test is made by adding to the filtered sample a strong solution of bleaching powder, which produces a brown precipitate or colour if any manganese is still present, in which case either more milk of lime must be added or a little more time given for that already added to react. When just sufficient lime has been added to remove all the manganese from the solution the addition is stopped.

The amount of lime so far added is always found to exceed that expressed by the simple equation

$$MnCl_2+Ca(OH)_2=Mn(OH)_2+CaCl_2,$$

because of the solubility of $Ca(OH)_2$ in $CaCl_2$ solution and because milk of lime always contains particles that react very slowly. The excess lime may vary from 0·10 to 0·45 (the theoretical lime given above being 1·00).

The amount of calcium chloride present profoundly alters the solubility (and hence the reactiveness) of the calcium hydrate, as is shown by the following figures for 60°C.:

Percentage $CaCl_2$ in solution .	0	5	10	15	20	25	30
100 c.c. dissolve g. of CaO . .	·09	·11	·13	·17	·22	·29	·38

On cooling very long crystalline needles of the oxychloride $ClCa·O·Ca·OH+7H_2O$ separate and so much so from strong, hot solutions that the mixture becomes apparently solid and can be inverted, and this has been assumed to be one of the reasons for the production of the "stiff batches" mentioned.

Starting from native manganese the liquor will contain about 18% $CaCl_2$ only, and because of the low solvent action of this concentration of calcium chloride on the excess lime already added, it is not permissible to add any further excess until some of the free lime has been removed by converting it into calcium manganite.

For this purpose the blast of air is increased to its maximum and continued until the end of the operation. The fixation of the oxygen causes the temperature to rise a few degrees, and the reaction $CaO+MnO+O=CaO·MnO_2$ reduces the amount of free lime and changes the colour of the precipitate from light yellow to brown, and then to black. After about a quarter of an hour one-fourth of the remaining excess lime desired is added, and these additions repeated after three more periods of blowing.

During the progress of the blowing, filtrates from samples will show a diminution and then the disappearance of the free lime. The simultaneous oxidations of the mixture ($CaO+MnO$) and of the excess MnO to form ($CaO·MnO_2$) and ($MnO·MnO_2$) respectively are now complete, and continued blowing has no further effect.

But by the addition of a second supply of manganese chloride liquor to the blowing tower a new reaction is now brought into play, namely

$$2(CaO·MnO_2)+MnCl_2 \\ =(CaO·2MnO_2)+CaCl_2+MnO,$$

and by continuing the air blast the MnO is converted into ($MnO·MnO_2$), as in the first part of the operation. The "blowing out" of the manganese becomes slower with each addition, and when it becomes too slow no more is added, and the whole operation is ended. The effect of this last operation is to increase the amount of chlorine that can be manufactured from the mud, without increasing the amount of acid required for its manufacture.

The mud, consisting of calcium dimanganite, $CaO·2MnO_2$, and manganese manganite, $MnO·MnO_2$, suspended in a calcium chloride solution is now run from the base of the oxidising tower by the cock and main *c*, *c*, Fig. 4, into the mud settlers C, C, similar in construction to the settlers A above. After a few hours the settling is complete and the clear supernatant calcium chloride liquor may then be run away through the main E, E, by opening the cock near the bottom of the tank and gradually lowering the swivel pipe *p*, until the black mud below is reached.

The manganese mud is now ready to be used in the manufacture of chlorine. It differs from native manganese in that it is entirely soluble in hydrochloric acid and that it dissolves very much more readily. The generating tank therefore does not require a false bottom, and it is made very large. Fig. 4 shows four such stills D, D, that may be 12 ft. diameter and 12 ft. deep. They are octagonal, but otherwise resemble in construction the native manganese still. The right-hand end still is shown in section, the two columns S, S are the perforated stone blocks for blowing in steam. The outlet liquor pipes are not shown, nor are the gas outlet pipes, nor the acid inlet pipes.

Into the still is charged any liquor available from the still E, because though it is not strong enough to act further on native manganese, it will act on recovered manganese mud, and this is one of the advantages of the Weldon process. Hydrochloric acid is then also run into the still till the acid liquors are 2 ft. deep. The settled mud in the settler tank C may then be stirred by a hand rake, to make it a little more fluid, and run through a cock *g* situated in the bottom of the settler, into the main *f*, *f*, and thence through another cock into the luted trap *h*, when it runs into the still. The chlorine is given off very readily, and the rate of evolution of the chlorine is governed by controlled addition of the mud. As the acid becomes exhausted steam is blown in to raise the temperature, and the further additions of mud are made with caution, until samples taken from the still by an earthenware cock (not shown), cease to be clear yellow and become a clear coffee colour that is not removed by further steaming. A sample tested with standard caustic soda solution will then show the presence of about 0·5% of free acid. The waste manganese liquor is now run, as before described, into a neutralising well G by opening an earthenware cock and the Weldon recovery process is repeated.

When sufficient mud has accumulated in settlers A, A, a long-handled plug (indicated by a dotted line in each of the tanks) is lifted, and the mud is run through pipes *q* to filter presses (not shown in the figure), where as much manganese chloride liquor as is possible is recovered, and the cakes of stiff, nearly dry mud are then thrown away.

When sufficient manganese chloride liquor has been made from native manganese in the still E to stock the settlers A and C, and to give working charges in G, B, and D, then only so much native manganese requires to be dissolved in E as will counterbalance the unavoidable losses in the whole of the Weldon plant.

(*b*) AIR OXIDATION.—*The Gaseous Hydrochloric Acid and Atmospheric Oxygen Method.*—After many unsuccessful attempts made by Oxland (1845), Jullion (1846), Binks (1860 and 1862), Dufrêne (1865), and others, the labours of H. Deacon and F. Hurter, from 1868 onwards, produced an entirely successful chlorine process which is based on the direct oxidation of the H in HCl by atmospheric oxygen, and which utilises much more of the HCl than any process employing either native or recovered MnO_2. Some processes patented later (Henderson, 1871; Weldon, 1871; Wigg, 1873, etc.) proceed on the same lines but have not been practically successful.

The Deacon process starts from the well-known fact that a mixture of hydrochloric acid gas and oxygen at a temperature just below a red heat, especially in contact with porous substances, partially changes into chlorine and water: $2HCl+O=H_2O+Cl_2$. This decomposition is very much assisted by the employment of substances which serve as oxygen-carriers, and of these the salts of copper (previously employed by Vogel, 1855; Gatty and Laurens, 1860; Mallet, 1866) have been found most useful. Probably in all cases cupric chloride is formed, which at once splits up into cuprous chloride and free chlorine. The Cu_2Cl_2 combines with oxygen to form oxychloride, $CuO{\cdot}CuCl_2$, and this acts again upon HCl, yielding water and reforming cupric chloride, so that the reactions can begin over again:

$$(1)\ 2CuCl_2=Cu_2Cl_2+Cl_2$$

$$(2)\ Cu_2Cl_2+O=Cl\text{—}Cu\text{—}O\text{—}Cu\text{—}Cl$$

$$(3)\ Cu_2OCl_2+2HCl=H_2O+2CuCl_2$$

Theoretically, all the HCl would thus be converted into chlorine, but in practice, under the best conditions, about two-thirds of this decomposition is effected. The undecomposed HCl is, however, not lost, but is recovered and can be utilised for other purposes, *e.g.*, for the Weldon process.

The reversible reaction of the Deacon process has been studied by Lunge and Marmier, by Lewis (J. Amer. Chem. Soc. 1906, **28**, 1380), and by von Falckenstein (Z. physikal. Chem. 1907, **59**, 313). Lewis and Randall ("Thermodynamics and the Free Energy of Chemical Substances," 1923, McGraw-Hill Book Co., Inc.) have critically examined these results and those obtained by Moldenhauer (Z. anorg. Chem. 1906, **51**, 369) for the hydrolysis and oxidation of magnesium chloride and have shown that all these results are in excellent agreement with the equilibrium constants calculated from the free energies of steam and gaseous hydrogen chloride, which are, of course, obtained by entirely independent methods.

For the reaction

$$\tfrac{1}{2}Cl_2(g.)+\tfrac{1}{2}H_2O(g.)=HCl(g.)+\tfrac{1}{4}O_2$$

they give the equation

$$\triangle F^\circ=6835-0{\cdot}02T\ln T-0{\cdot}00085T^2 \\ +0{\cdot}000000185T^3-7{\cdot}27T,$$

where $\triangle F^\circ$ is the change in free energy.

From the equations

$$K=\frac{[O_2]^{\frac{1}{4}}[HCl]}{[Cl_2]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}}$$

and $$-RT\ln K=\triangle F^\circ$$

the equilibrium constants may be calculated. Although the equilibrium equation is in terms of activities, pressures (as atmospheres) may be used as a first approximation.

The following figures are calculated from Lewis and Randall's equation:

Temp. °C.	300	350	400	450	500	550	600
$\triangle F^\circ$ cals.	2,350	1,940	1,525	1,110	690	270	−154
K. . .	0·13	0·21	0·32	0·46	0·64	0·89	1·09

Deacon's process deals with the gaseous hydrochloric acid, as it is evolved in decomposing common salt by sulphuric acid without condensing it into liquid acid. In practice only the gases from the decomposing pots, say 68–70% of the total HCl, are used for the Deacon process, those coming from the roasters being too dilute and containing too much sulphuric acid.

The quantity of air necessary to form chlorine enters through the joints of the doors and dampers and is regulated by the suction maintained on the whole plant. Usually there are 4 vols. of air to 1 vol. of HCl. An excess of air is less injurious than a deficiency of it, in which case there is a poor decomposition.

The gases leaving the pot are first cooled by a long string of pipes and a scrubber; thus much of the water and about $\frac{1}{6}$ or $\frac{1}{5}$ of the HCl are removed. Further, the gas may be dried in a sulphuric acid tower before it enters the decomposer, such complete drying being very advantageous for the process. The gases now enter the heating furnace in which pipes are arranged in two sets of twelve.

The gases are here heated up to 500°; the waste heat of the furnace is sufficient for heating the decomposer, which does not possess any fire of its own.

The gases now pass into the decomposer (Fig. 5), an upright, cast-iron cylinder. It contains a cylindrical ring of broken bricks D, D, supported by two cylindrical cast-iron rings of shutters placed concentrically one within the other. The gases enter at the circumference at A, pass radially across the decomposing mass D into the inner space, and are led away through the pipe OB. The decomposer temperature ought to be between 480° and 500°. The catalyst mass consists of burnt clay broken up into lumps, or ordinary bricks broken, freed from dust, and dipped into a solution of cupric chloride. The mass contains about 0·6–0·7% of metallic copper.

When the gases leave the decomposer, they consist of a mixture of HCl, free Cl_2, and steam. At best two-thirds of the HCl is converted into chlorine, but sometimes only one-half. The hot exit gases are now cooled by passing through a long string of earthenware or glass pipes, and are then freed from HCl by washing with water in the ordinary acid condensers, consisting of stone towers filled with coke, combined in some works with acid cisterns. Woulff's jars, etc. By properly managing this process, all the acid can be obtained in the state of concentration required for the Weldon process and other purposes.

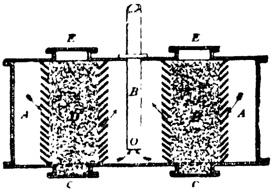


Fig. 5.

There is theoretically no loss of HCl in the Deacon process, the whole of the acid evolved from the salt being either converted into chlorine or recovered by condensation as aqueous hydrochloric acid. In practice, of course, some losses occur, but they are not necessarily large.

During the early years of the working of the Deacon process results were disappointing and unsatisfactory. The fact that impurities accompanying the gaseous HCl were sufficient to seriously affect the process was not realised. The impurities are sulphuric and sulphurous acids, arsenious acid, water, and carbon dioxide. The arsenious acid, derived from the As_4O_6 in the sulphuric acid used, forms arsenate of copper, which is even less reactive than the $CuSO_4$ formed from the sulphuric acid impurity. The presence of these impurities necessitated the frequent renewal of the decomposing material. Water is one of the products of the decomposition, and hence, when present in the inlet gases, increases the partial pressure of the products of the reaction and lowers the maximum percentage decomposition obtainable under the conditions of the process.

Carbonic acid derived from the fuel gases, either of the salt-cake furnaces or of the decomposing furnace itself, was a serious obstacle to, and frequently entirely prevented, the production of strong bleaching powder. This difficulty has been overcome by greater care in the construction of the apparatus and in testing for leakage.

It will be noted from the above description that only the gaseous HCl from the salt-cake pot is dealt with by the Deacon process, and the liquid acid collected after the decomposers has to be sold as such or used in some other way, such as by the Weldon process.

Hasenclever, however (B P. 3393, 1883), described a process for gasifying the HCl in the liquid acid by mixing with strong, hot sulphuric acid in a series of earthenware vessels through which air is blown. By this means a steady, continuous stream of gaseous HCl is evolved with an easily regulated supply of air. After passing through the series of vessels, the vitriol diluted with the water contained in the liquid hydrochloric acid has to be reconcentrated to the original sp.gr. The concentration is generally performed in long, lead, bricklined pans, heated by top heat, the fuel gases being in direct contact with the sulphuric acid. This process was used to a considerable extent, but from the large quantity of sulphuric acid to be concentrated per ton of bleaching powder, a very material addition is made to the cost of manufacture.

Other Contact Substances.—A general investigation on the mutual action of HCl and O in the presence of certain compounds of Cu, Fe, Mn and Cr was made by Lamy (Bull. Soc. chim. 1873, [ii], **20**, 2). Copper salts were found to be more efficient than others, and with these the decomposition is at its maximum at about 440°.

The proposals to employ ferric chloride (Thibierge, 1855, and others) or chromic oxide (Hargreaves and Robinson, 1872) have not had any practical success.

Nickel oxide was proposed by L. Mond (B.P. 8308, 1886).

De Wilde and Reychler (B.P. 17272, 1889) proposed employment of a mixture of magnesium and manganese chlorides with magnesium sulphate.

Production of Chlorine by Electrolysis of Alkali Chloride.

Technical. Theoretically a current of 1 amp. liberates in 1 hour $\text{g.}\,\frac{\text{equivalent}\times 3{,}600}{96540}\,\text{g.}$ of an element.

Simple as the electrolysis of alkali chlorides may appear from the formula, yet in aqueous solutions the first obvious difficulty arises from the activity of the alkali metal. Where no attempt is made to separate the cathode and anode products, the output of such a cell will be hypochlorite or chlorate according to the conditions of operation.

The separation of the two products naturally presents many difficulties, since factors such as temperature, electrolyte concentration, ionic mobility, electrode materials, and current density play an important part.

The effect of two of these factors is shown by the fact that the conductivity of solutions of alkali chlorides increases with concentration and with temperature.

The voltage of an electrolytic cell depends on the decomposition voltage of the salt, the length of the electrolytic path, the overvoltage at each electrode, and the current density of the cell. In the case of a diaphragm cell, resistance of the diaphragm is also a factor.

Thomson's formula may be used to calculate the approximate decomposition voltage (E) of a salt: $E = \frac{Q}{n \times 0{\cdot}2387 \times 96{,}540}$, where Q is the heat of formation and n is the valency.

Overvoltage is an inherent property, non-calculable, of the electrode material. Although the hydrogen over voltage in caustic solutions at graphite electrodes is very low, for constructional purposes metal cathodes are preferable and nickel with a low hydrogen over voltage is suitable, but iron with a slightly higher over-voltage, 0·08 volt (Caspari), is cheaper.

Mercury is in a class apart with a very high hydrogen over-voltage, 0·78 volt (Caspari), 1·0 volt (Tafel), and it is due to this property that sodium is discharged preferentially on electrolysis in the mercury cell process and that sodium amalgam is only very slowly decomposed by water. This fundamental property has made possible the development of the mercury cell.

Chlorine over-voltage also varies with the anode material: at carbon electrodes it is low, whilst at platinum or fused magnetite it is high.

The following determinations of single electrode potentials may be noted:

OH'	ion discharge	+0·82 v.
Cl'	,, ,,	+1·37 v.
$H^{\cdot}$	,, ,,	−0·41 v.
$Na^{\cdot}$	,, ,,	−2·71 v.
$Hg_nNa^{\cdot}$	,, ,,	−1·81 v.

In a brine solution the smallest decomposition voltage is 1·23 for the electrolysis of water, but the over-voltages are high and at higher voltages little of this process proceeds.

At 4·08 volts electrolysis of anhydrous sodium chloride commences, but since in aqueous solution the exothermic reaction between sodium and water to give caustic soda and hydrogen takes place, the decomposition voltage will be reduced. It will be higher than the decomposition voltage of hydrochloric acid, 1·78 volts, due to the fact that hydrogen ion concentration will be low at an electrode where there is a preponderance of OH' ions from the caustic soda and there is a rise in the single potential for hydrogen ion discharge. The decomposition voltage will depend on the strength of the caustic soda as well as that of the brine, but is of the order of 2·2 volts.

With a dilute sodium amalgam cathode the single potential of sodium is lowered by reason of its solubility in the amalgam, and the decomposition voltage is of the order of 3·18 volts.

The decomposition voltages, therefore, of sodium chloride in saturated brine are approximately 2·2 volts for diaphragm cell processes and 3·2 volts for mercury cell processes.

The mobility of ions plays an important part in diaphragm cell processes. The hydroxyl ion with a potential drop of 0·1 volt at room temperature has a velocity of 6·48 mm. per hour compared with 2·41 mm. per hour for chlorine. Migration of hydroxyl ion, therefore, must be opposed by a suitable velocity of electrolyte through the diaphragm if satisfactory yields are to be obtained. It becomes clear, then, that for the same efficiency horizontal diaphragm cells will yield a stronger caustic liquor than vertical diaphragm cells.

The choice of materials for electrodes has been limited in course of time by initial cost and by running costs. The high over-voltage and high cost of platinum and magnetite anodes have eliminated these from chlorine cells and artificial graphite is now universally employed. This latter material, which is porous by reason of its method of manufacture, suffers from the fact that as porosity increases so the life of the anode decreases. It has been contended that in the pores where there is no appreciable circulation, the aqueous solution becomes depleted of chloride ion and hydroxyl ion discharge occurs; this results in oxidation of the anode to carbon dioxide and disintegration is promoted.

Cast magnetite (G.P. 157122 and 193367, GriesheimE-lektron) was used to overcome the defects of porous carbon, and with particular advantage in the Griesheim cell, where the chlorate concentration in the anolyte accentuated attack on the carbon.

More recently attempts have been made to increase the life of graphite anodes by impregnating them with organic substances to reduce their porosity (Fitzgerald and Molloy, B.P. 1376, 1872; Atkins, U.S.P. 754114, 1904; de Vains, F.P. 567925, 1922; Koholyt, B.P. 221634, 1923; Pomilio, Giorn. Chim. Ind. Appl. 1925, 7, 63; Bozel-Maletra, F.P. 679816, 1928). Jaffe (Z. Elektrochem. 1936, **42**, 71–85) shows that impregnation causes an increase in the over-voltage of chlorine discharge.

DIAPHRAGM CELLS.—*The Griesheim Cell.*—This was one of the earliest cells to be operated on an industrial scale, although it has now been replaced largely by more economic units. It employs stationary electrolytes and, therefore, has not the same intensity of output, nor the same economy in power and materials as later cells, but its advantages of robustness and simplicity well fitted it for the early days of electrolytic chlorine production. It depends essential on Breuer's diaphragm (B.P. 19775, 1891) made by setting cement with acidified brine; after complete setting the crystallised salt can be washed out to leave a very porous block.

A number of boxes made of such diaphragm plates fixed in an angle iron frame rest in an outer steel container. These boxes make the anode compartment which is fitted with carbon anodes, whilst the steel outer vessel and steel plates hung between the boxes form the cathode. Porous pots filled with salt are suspended in the anode chambers to maintain the strength of the brine. Fig. 6.

The method of operation is to fill the anode compartment with saturated brine and the outer container with weak brine. As electrolysis proceeds alkali accumulates in the cathode liquor until the concentration reaches 40 to 50 g. of caustic soda per litre, when electrolysis is stopped, the caustic liquor drained off, and after refilling the cathode chamber the process is recommenced. In its long history the cell has naturally undergone many changes, bigger cells were made and provision was made for maintaining a high working temperature and for collection of hydrogen.

The cell voltage was of the order of 3·65, with current densities at the anode of 2 amps./dm.^{2}, and at the cathode of 0·5 amps./dm.^{2}

Owing to the low output and absence of positive movement of solution through the diaphragm, back diffusion of hydroxyl ion is appreciable. This leads to low efficiencies, high chlorate content, and rapid anode attack. This latter results in a high carbon dioxide content of the chlorine which in turn causes difficulty in bleaching powder production. Attempts to obviate these difficulties led to the manufacture of magnetite electrodes, but these add appreciably to power consumption owing to the much higher chlorine over voltage.

This cell was largely applied to the electrolysis of potassium chloride in Germany.

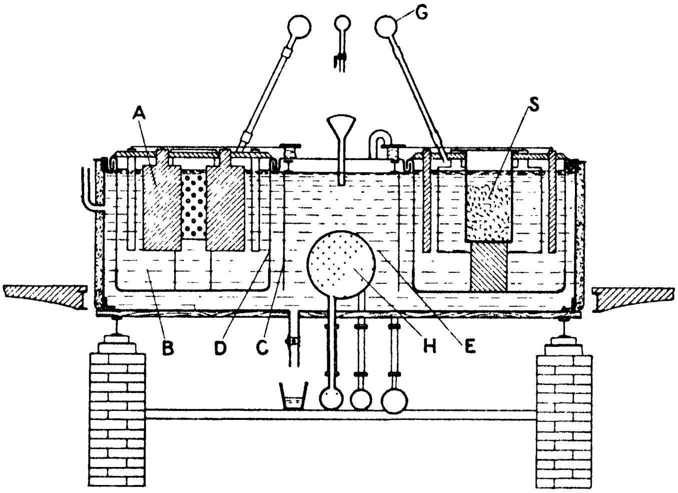


Fig. 6.

The Siemens-Billiter Cell.—The first installation of these cells was tested in 1907 at Aschersleben by the association of Kaliwerke Aschersleben, Siemens & Halske A. G., Billiter, who had carried out much experimental work previously in Vienna.

Many plants were subsequently erected in Germany.

The cell consists of a sheet iron tank, the cathode is a sheet of perforated iron or iron netting attached to the walls a little above the bottom of the cell.

The side walls above the cathode are covered with a layer of cement, whilst the cover of the cell consists of tiles of concrete or stoneware. The anode leads of graphite which carry graphite plates pass through the cover, whilst the iron shell is connected to the cathode leads. The chlorine outlet in the cover is connected to an earthenware main, whilst an outlet pipe of iron from the cathode chamber serves to carry away the hydrogen. The caustic liquor drains from the cathode chamber continuously. Fig 7.

The cell is the only type in large scale commercial production which has a horizontal diaphragm and the success depends on having a suitable diaphragm which has sufficiently fine capillaries and at the same time a readily regulated porosity. The essence of Billiter's diaphragm is the use of a fibrous material, asbestos, and a powder, barytes, which are spread uniformly on a sheet of asbestos cloth resting on the cathode. With a suitable diaphragm there is no tendency for hydrogen to penetrate, and the avoidance of this eliminates the difficulty of producing a satisfactory chlorine as well as a caustic liquor of constant and suitable composition.

The cell having been filled with brine, the circuit can be closed. The brine percolates uniformly through the diaphragm, and as the anodes practically cover the whole diaphragm a uniform current-distribution and brine-flow ensue.

A level gauge is fitted to the side of the cell to indicate the depth of brine, but a modification has been introduced in recent years. A small vessel external to the cell is connected to it just above the diaphragm and the hydrogen from the cathode chamber bubbles through the brine in this vessel. By varying the depth of the hydrogen seal in the brine the rate of brine percolation through the diaphragm is controlled at the desired rate under varying conditions of hydrogen and chlorine pressure and of brine level.

In actual construction the tank may be shallow, little deeper than the cathode compartment, and the wall of the cell may be built up of brick or stone suitably tied together.

The cell is operated to give a constant alkalinity which is achieved by varying the level of brine in the cell. The rate of percolation and the cell voltage remain practically constant for many months, but gradually the diaphragm becomes blocked owing to the accumulation in it of calcium and magnesium deposits, and the cell is then cut out for cleaning. The depth of brine, which may be 8 cm. at the commencement of the cell life, will be gradually increased during the run, possibly to 24 cm. when cleaning is due.

The results of a run of two months with brine not specially purified are given by Billiter.

Mean current . . .	2001·6 amps.
,, ,, efficiency	94·7%
,, voltage . . .	3·66 v.
,, alkalinity . .	130·2 g. $NaOH$/litre.
CO_2 content of chlorine	1·17%

The average voltage for different current densities of a cell working at 85°–95°C. is :

Current density amps./dm.^{2}	4·6	7·0	10·0
Voltage	3·5	4·0	4·7

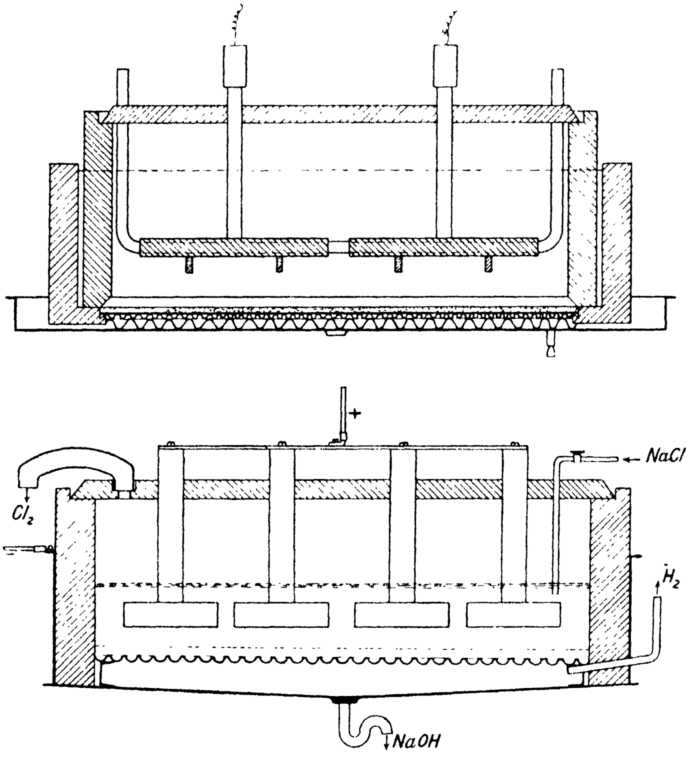


FIG. 7.

The alkali content of the cathode liquor is 12–16% for $NaOH$ or 18–20% for KOH with average current efficiency of 95%.

The Bell-jar (*Aussig*) *Cell.* Fig. 8.—This cell, formerly operated by the Verein für Chemische und Metallurgische Produktion at Aussig, Czechoslovakia, is sometimes known as a gravity cell. It may be described as a diaphragm cell which dispenses with a solid diaphragm, since it functions by reason of stratification of the liquors. The density of the caustic liquor produced at the cathodes outside the bell-jar is slightly greater than that of the feed brine, and the flow of brine from the anode in the bell to the cathode counteracts the tendency for alkali to diffuse back to the anode.

In a concrete vessel 8 to 10 ft. long, 4 ft. wide, there rest 25 bells ; the bells, which are long and narrow, are made of sheet iron coated inside with cement, and rest on a ledge in the concrete wall. The graphite plate anodes lie horizontally inside and just above the lip of the bell and the brine feed is distributed uniformly above the anode. The sheet iron bell acts as cathode and the caustic liquor overflows continuously.

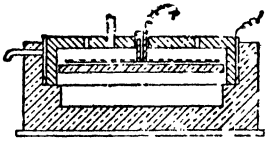


FIG. 8.

The cell is reputed to have a long life. Each bell takes 20 amps. at a voltage, increasing from 3·7 to 4·2 during a run, and the cell has a current efficiency of 85–90% when producing a caustic liquor containing 120–140 g. $NaOH$ per litre.

The Billiter-Leykam Cell.—This cell was devised as an improved bell-jar cell. The cathode is placed below the bell and consists of **T**-section iron bars which are enclosed in tubes of asbestos cloth. The cloth is not an electrolytic diaphragm, since its purpose is solely to keep the hydrogen separate and carry it from the cell so that the chlorine may not be contaminated and the caustic liquor may not be agitated.

At 85°C. the voltage is 3·2, caustic liquor 150 g. $NaOH$ per litre with current efficiency 92–94%.

The cell was intended by Billiter as a trouble-free unit for small operators.

The Gibbs Cell.—This cell dates from about the same time as the Siemens-Billiter and has found its principal applications in America. It was followed by the Vorce and Wheeler cells, which are derived cells different in detail.

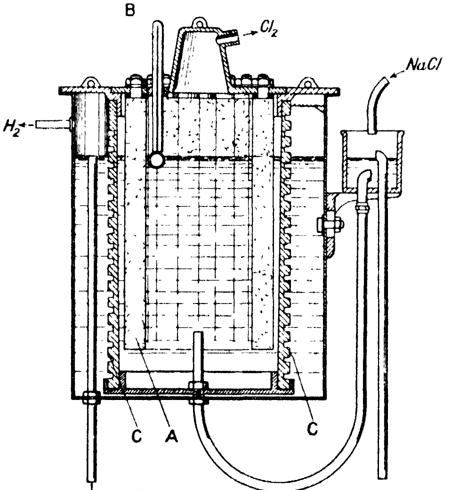


Fig. 9.

The diaphragm here is vertical and cylindrical (Fig. 9). The cathode is a perforated steel cylinder closed at the bottom and top with a cement disc and cover respectively. The diaphragm of asbestos paper rests inside the cathode and the anodes of carbon rods inside the shell are suspended from the cover. The cell rests inside a cast-iron or steel cylindrical tank, this forming the cathode compartment.

The original patent indicated the cathode compartment flooded with caustic liquor; this method of working was abandoned in favour of a drained cathode, which is reminiscent of the much earlier Hargreaves-Bird cell.

The Hargreaves-Bird Cell.—This cell, like the Griesheim cell, is interesting historically as being one of the first to achieve commercial success. It is particularly interesting as the progenitor of the continuous type with vertical diaphragm and drained cathode which has achieved greatest success.

It was operated by Electro-Bleach & By-Products, Ltd., at Middlewich, England, until 1928, when the works was closed down.

The cell consists of a cast-iron container, 7 ft. high, 11 ft. long, 1½ ft. wide, lined with cement or brick. It is divided into three compartments, by asbestos cement composition diaphragms fixed to copper mesh cathodes; the anode compartment is between the two cathode compartments. Fig. 10.

Although caustic soda was made in this cell, in practice steam and carbon dioxide were blown into the cathode compartment and sodium carbonate was produced.

The later cells of this type adopted newer materials and improved methods of construction which gave a greatly increased output.

The Allen-Moore Cell.—This, like its forerunner, the Hargreaves-Bird cell, is rectangular with vertical diaphragms. A concrete monolith makes the bottom, top, and ends of the cell, the sides being closed by shallow steel boxes which bolt on to the concrete. The cell thus formed contains the perforated steel sheet cathode on which rests the asbestos diaphragm.

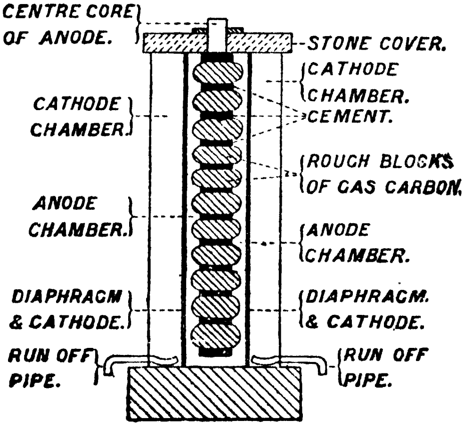


Fig. 10.

The graphite anodes pass through the concrete top, and the asbestos diaphragms inside the steel boxes bolted to the concrete form the anode chamber. Fig. 11.

The standard unit takes 1,200 amps. at an average voltage of 3·55. The caustic liquor, 80–100 g. $NaOH$ per litre, is produced with a current efficiency of 95%. The diaphragm life is 3 months and anode life 18 months.

The cell is principally used in paper mills in U.S.A.

The Townsend Cell.—This is similar to the Allen-Moore cell. A new idea is introduced in the flooding of the cathode chamber with kerosene. This compensates the hydrostatic head of brine on the opposite side of the diaphragm and reduces the rate of percolation. The production of a stronger caustic liquor is possible without the back diffusion of the OH' ions into the anolyte having quite the same force as if the cathode were submerged in caustic liquor completely. The caustic liquor is carried away from the cathode by the hydrogen, and sinks through the kerosene and runs away. Fig. 12.

A standard 2,500-amp. cell is 8 ft. long, 1 ft. wide, and 3 ft. deep. The caustic liquor, 150–180 g. per litre, is produced at a current efficiency of 95%, the cell working at 4·0 to 4·2 volts.

The diaphragm of asbestos cloth is painted with a mixture of asbestos fibre, ferric oxide, and colloidal ferric hydroxide.

This cell is operated by the Hooker Electrochemical Company at Niagara Falls.

The Pomilio Cell.—This cell is very similar to the Townsend and other cells of this type. It operates with a controlled submergence of the cathode. The depth of caustic liquor is altered as required to control the rate of percolation. A 3,000-amp. cell at an average voltage of 4·0 produces a caustic liquor of 140–170 g. NaOH per litre.

The first installation was made in 1921 at Naples.

The Nelson Cell.—This is a diaphragm cell consisting of a rectangular steel box in which a U-shaped perforated steel sheet is attached to the top ; the ends of the channel are closed by the ends of the steel box which must, therefore, be protected inside the anode compartment by cement or concrete. The diaphragm consists of sheets of asbestos paper and the graphite anodes, 14 to the cell, are blocks 4 in. by 4 in. by 17 in.

A cell normally works at 1,000 amps. with a voltage of 3·75, and produces caustic liquor containing 90 to 100 g. per litre.

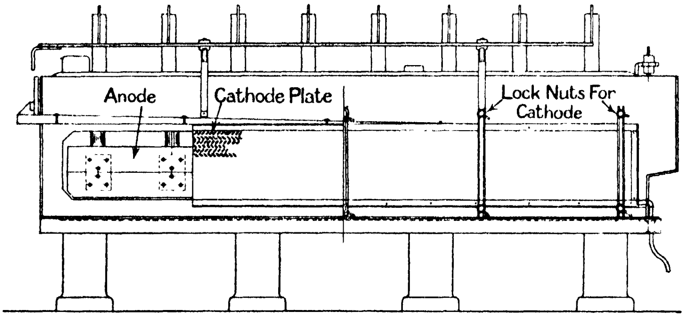


Fig. 11.

This cell was adopted for what was at one time the largest alkali-chlorine plant in the world, the Edgewood Arsenal plant of the U.S. Government.

The Krebs Cell.—This is an improved multiple Nelson cell with two or more U shapes in the diaphragm. The double U diaphragm cell takes 2,000 amps. Means are provided for increasing the depth of electrolyte as the rate of percolation tends to decrease. At 90% efficiency a cathode liquor averaging 110 g. NaOH per litre is produced.

Several installations of this cell have been made in Europe.

The Basle Cell (Ciba, Monthey).—Known by several names, this is the cell of the Society of Chemical Industry in Basle and is operated at Monthey in Switzerland and in several installations in Italy and France. It is a cell of novel design and possesses two diaphragms which it is claimed give long anode life, low hydrogen content of the chlorine, and good efficiency.

The cathode is a cylindrical iron wire cage of small diameter, 24 in. long, on which the asbestos diaphragm is deposited externally. The bottom of the cylinder is closed whilst there is a restricted outlet, of ½-in. I.D. iron pipe, so that a froth of hydrogen and caustic liquor is carried upwards into a closed channel in which they can separate.

The anode is a carbon plate which is surrounded by an asbestos cloth hanging from the cell cover. The plate, 24 in. by 4 in. by 2 in., is drilled and screwed at one end to receive the anode current lead which is a carbon rod 1½ in. diameter.

A cathode unit consists of twelve cathodes attached to the closed channel and the anode unit consists of ten anode plates attached to the cell cover, an inverted earthenware trough, which serves to collect the chlorine.

Cathode units alternate with anode units in the cell container, individual cells carrying 6,000 amperes.

The reported performance is current density 4·5 amps./dm.^{2} at the anode and 9·0 amps./dm.^{2} at the cathode, starting voltage 3·3 v. rising to 4·5 v., caustic liquor 110–130 g. per litre with current efficiency of 93%.

The Gauss Cell (Badische Anilin- und Soda-Fabrik).—Little, beyond the patent specification, has been published regarding this cell, but it is reported to be worked on a large scale. Similar to the Basle cell in having two diaphragms, it is, however, so arranged that the brine feed is divided, and a portion of the main feed to the anode compartment is bled off to the space between the diaphragms.

The object of this arrangement is to reduce the back diffusion of hydroxyl ion to the anode compartment, with corresponding diminution of the conversion of dissolved chlorine to hypochlorite.

The Finlay Cell.—In this double diaphragm cell the brine feed is introduced between the diaphragms. Successful operation depends on reducing the electrolyte gap which was achieved by a sort of filter press arrangement. The tendency for the anolyte to become denuded of chlorine ion would appear to be compensated by resaturation of the effluent brine.

Mercury Cells.—*The Castner Cell.*—This cell shares with the Griesheim, Le Sueur, and Hargreaves-Bird cells the position of being one of the first cells to prove successful on the industrial scale. It is described as consisting of a box, A, 4 ft. square, 6 in. high, with two vertical partitions which divide it into three equal compartments. The whole is constructed of slate or concrete. There is a gap under the partitions of $\frac{1}{16}$ in. and a corresponding channel in the cell bottom which has been filled with mercury effectively seals the compartments but allows a flow of mercury. Fig. 13.

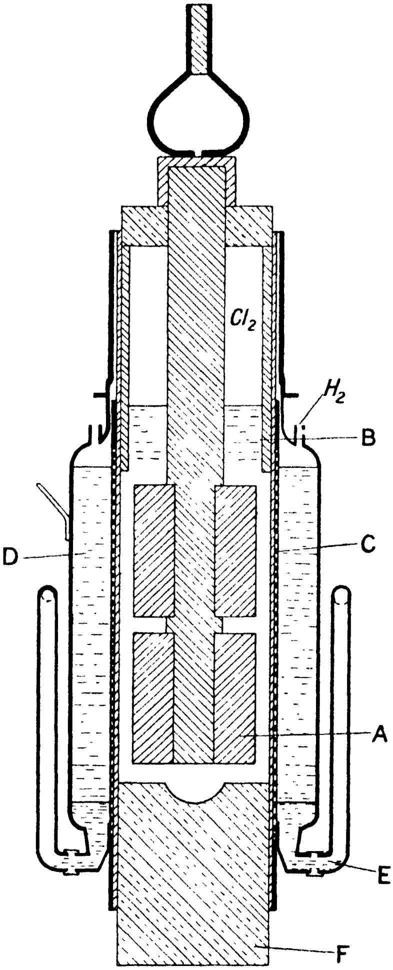


Fig. 12.

Foerster gives the cell performance as 630 amps. at 4·3 volts.

In the two outer brine compartments chlorine is evolved, whilst in the inner compartment sodium amalgam is decomposed and caustic soda produced.

Mercury circulation is effected by oscillation, one end of the cell resting on a fixed support, B, the other being attached to an eccentric, C, which by its rotation imparts a rise and fall, with an amplitude of half an inch.

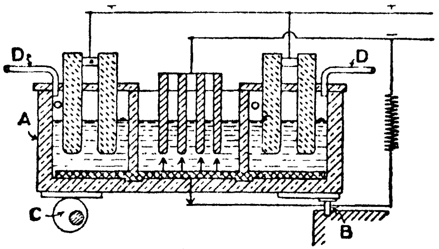


Fig. 13.

The anodes consist of graphite rods which enter through the side of the cell, and the original proposal for the cathode was an iron grid suspended in the caustic soda. This arrangement, which makes the mercury a bipolar electrode, was never worked, since for continuous operation each side of the bipolar electrode must work with the same efficiency. Castner, in the attempt to reduce power consumption to a minimum by using this arrangement, balanced the loss in the brine cell by a regulated shunt between the iron cathode and the mercury. Finally, however, the mercury was made the cathode, and the discharge of sodium from the amalgam was achieved as in the Kellner cell by making the caustic compartment into a short-circuited primary cell with an iron cathode.

The Kellner Cell.—The construction of this cell in three compartments is similar to that used by Castner except that the cell is fixed and the mercury is caused to circulate to and fro by means of air pumps. Compressed air blown alternately into iron bells, D_1 and D_2, immersed in mercury troughs outside each end of the cell effects the regulated displacement and flow of mercury.

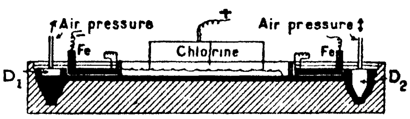


Fig. 14.

The centre compartment serves for the decomposition of brine, whilst caustic soda is produced in the two outer compartments.

The cell is made of concrete 12 ft. long by 3 ft. 6 in. wide, and the anode chamber formed by slate partitions is 5 ft. 6 in. long. The anodes of platinum wire net, 88 in number, each weighing 1 g., are mounted in concrete. The caustic soda is produced in the outer compartments using cast-iron grids as the cathodes of a short-circuited primary cell. Fig. 14.

The cell takes some 4,000 amps. at 5 volts giving a cathode current density of 25 amps./dm.^{2} Working at 50°C. there is a current efficiency of 92% and the caustic liquor contains about 30% $NaOH$.

The cell is operated by the Bosnische Elektrizitäts A.-G., at Jajce, in Jugoslavia.

The Whiting Cell.—A small installation of this cell has been operated by the Oxford Paper Company, U.S.A. (U.S.P. 951228, 951229 of 1910).

A shallow cement box is divided into five compartments by glass partitions to form the cell proper. As electrolysis proceeds, the amalgam of each compartment in turn is discharged into a single caustic compartment where it follows a serpentine path down channels in graphite blocks in contact with caustic liquor. After removal of the sodium the mercury is elevated from the sump to a reservoir which recharges the brine compartments in turn.

Working at 40°C. with a current efficiency of 90–95%, a 20% caustic liquor is produced (Whiting, J.S.C.I. 1910, **29**, 436).

The Wildermann Cell.—This cell has been operated in Germany. Its outstanding feature is the quasi-vertical arrangement of the mercury cathode. To provide this a series of Y section ring-shaped channels are mounted one above the other and mercury is filled into each trough so that the lower leg of the Y section dips into the mercury in the ring below. These rings of iron are covered with ebonite. The system of ring channels makes a cylinder which is mounted in a container. The cylinder is the brine compartment and the annulus the caustic soda compartment. Inside the cylinder and as close as possible to the ring channels are vertical graphite anodes. The mercury is agitated by means of teeth at the end of arms which pass between the anodes, the arms being attached to a central shaft which is actuated to give rapid vibration. The whole of this mechanism is covered with ebonite. Fig. 15.

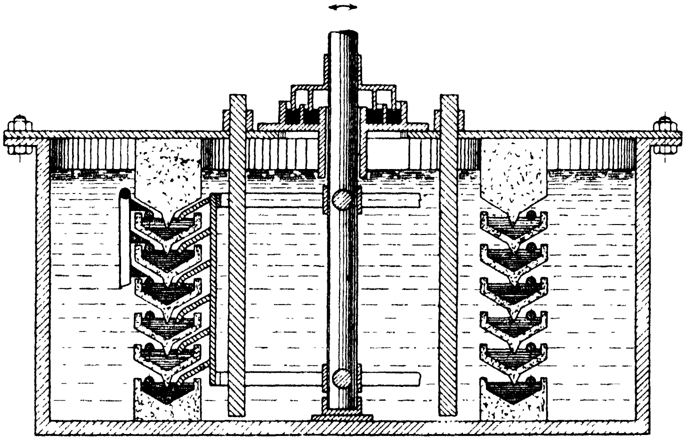


FIG. 15.

Graphite rods floating in the amalgam in the caustic compartment assist in discharging the sodium from the amalgam.

A 6,000-amp. cell covers an area of 32 sq. ft. and works at 5 volts with cathodic current density of 20 amps./dm.^{2} at a temperature of 50°C. ; 25% caustic soda liquor is produced.

The Kellner-Solvay Cell.—The form in which the mercury cell has found widest application is the Kellner-Solvay cell. It is operated in several slightly differing forms, chiefly in Great Britain and on the Continent.

The cell consists of two concrete troughs side by side, each with a slight slope in opposite directions, covered when working with a sheet of mercury or amalgam.

In the brine compartment electrolysis takes place between either platinum or graphite anodes and the mercury cathode. Chlorine is removed through a suitable exit and sodium amalgam is discharged into the caustic compartment where it is decomposed by a counter current of water with liberation of hydrogen. Fig. 16.

The mercury, stripped of its sodium, is elevated back to the brine compartment, to begin the cycle afresh, by means of a scoop-wheel (Solvay), Archimedean screw (Castner-Kellner), or vertical screw (Aussig) (Taussig, Z. Elektrochem. 1909, **15**, 659).

A circulation of brine is maintained between the cells and the salt saturators.

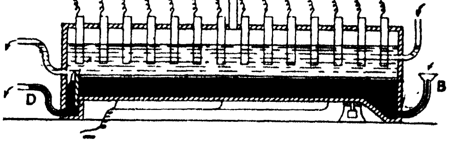


FIG. 16.

According to Foerster, this cell consists of a cement-lined iron container 14 m. long by 50 cm. wide which, according to Billiter, takes 12,000 amps. at 5 volts using platinum anodes. The loss of platinum is given as about 1½% per annum.

The chlorine gas, using platinum anodes, contains 99·6% chlorine, 0·2% hydrogen, and 0·1% oxygen, whereas using carbon anodes it contains 96% chlorine, 3% hydrogen and 1% carbon dioxide.

The chief advantage of the mercury process is the higher concentration of the caustic liquor of greater purity. The disadvantages are the higher power consumption, the large amount of capital invested in mercury, and the high percentage of hydrogen in the chlorine.

Whilst the mercury process is used almost exclusively in the production of caustic soda, it may be used for the production of caustic potash, but with greater difficulty, *see* Allmand and Ellingham, " Applied Electrochemistry," 1924 ; Kurt Arndt, " Technische Elektrochemie," 1929 ; Engelhardt, " Handbuch der Technischen Elektrochemie," 1931 ; Foerster, " Elektrochemie wässeriger Lösungen," 1922 ; Billiter, " Die elektrolytische Alkalichloridzerlegung mit starren Metallkathoden, i, 1912, ii, 1913 " ; Lucion, " Die elektrolytische Alkalichloridzerlegung mit flüssigen Kathoden," 1906.

Cells with Fused Electrolyte.—The Vautin cell (B.P. 13568, 1893, and 9878, 1894) electrolysed fused $NaCl$ or KCl, with or without the addition of fluorides or other chlorides to lower the point of fusion, over a cathode of molten lead or tin with which the sodium or potassium formed an alloy (*see* paper by Vautin, J.S.C.I. 1894, **13**, 448).

The Acker cell is designed on the same principle as the Vautin cell, and makes use of the lead cathode (*see* B.P. 6636, 6637, 1898). Below is a sketch (Fig. 17) of the Acker cell, taken from a paper by J. B. Kershaw in Electrician, 1902, *48*, 20. The bottom of the cell P is trough-shaped and of cast iron. It serves as electrical connection between the main conductor and the mass of fused lead L resting on it. The upper part of the cell Q is constructed of any refractory basic material not attacked by chlorine gas or fused salt. The anode C is of carbon and dips into the fused salt. The channels and subsidiary vessel R are arrangements designed to remove and decompose the lead alloy as it becomes sufficiently saturated with sodium. The decomposition of the alloy is effected by blowing steam into it, and the heat generated by the conversion of the sodium into hydroxide is returned to the cell and assists in maintaining the necessary temperature. The voltage actually taken by the Acker cell is 6·75, and the current efficiency 54% ("Report of Commission on Science and Arts," J. Franklin Inst. 1903, **156**, [3] 221–4). The Acker cell was worked at Niagara Falls on an industrial scale from about 1900 to 1907, when the works were completely burned down and have not been rebuilt. Fig. 19.

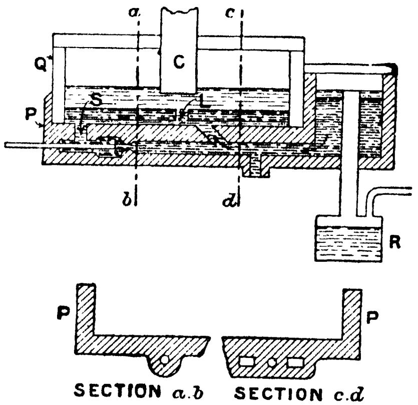


FIG. 17.

The Ciba cell (Fig. 18) is used for the production of sodium by the electrolysis of fused sodium chloride, the production of chlorine being incidental thereto.

It is described by Gesellschaft für Chemische Industrie (B.P. 18300, 1910, and 17047, 1911) as constructed of fireproof brick so arranged that the chambers for collecting the products of electrolysis are separated from each other by walls or diaphragms which are mainly vertical and are capable of resisting attack by the electrolyte and the products of electrolysis.

The salt, which may be molten alkali chloride or mixtures thereof with other salts, is fused by an arrangement of heating resistances and additional electrodes for melting the electrolyte by alternating current, the resistances being used to produce a layer of molten salt.

The Downs cell for the production of alkali metals and chlorine is described by the Roessler and Hasslacher Chemical Company of New York (B.P. 238956, 1924) as one in which the metal halide salt is first heated, fused, and thereby freed from moisture in a large, separate compartment of the cell before it is subjected to electrolysis in the second compartment which is the cell proper.

The anode is preferably graphite, the cathode is either iron or copper, and these are substantially concentric, whilst the cell container is a steel shell lined with suitable refractory bricks.

The electrolytic compartment is formed by a combination of the sodium collector and the chlorine collector from which two concentric diaphragms are suspended. The collector combination is submerged in the molten electrolyte and the sodium flows continuously from the collector up a riser pipe to a receiver. The upper portion of the chlorine collector is of reduced cross section, so that above the collectors a considerable volume of molten salt is provided by the fusion compartment, and by this means access of moisture or gaseous impurity into the cell proper is avoided. Fig. 20.

See also Billiter, "Schmelzfluss-Elektrolyse" Knapp, 1932.

ELECTROLYSIS OF ZINC CHLORIDE.—The waste calcium chloride from the ammonia soda process was utilised from 1897 for some years by Brunner, Mond & Co., of Winnington, as a source of chlorine. The process has now been discontinued. By heating the liquor with crude zinc oxide and carbon dioxide the reaction

$$CaCl_2+ZnO+CO_2=ZnCl_2+CaCO_3$$

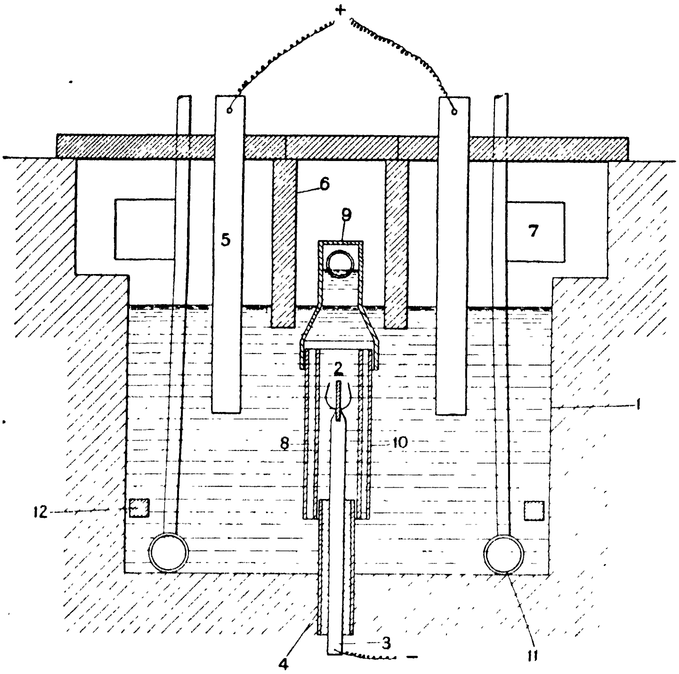


Fig. 18.

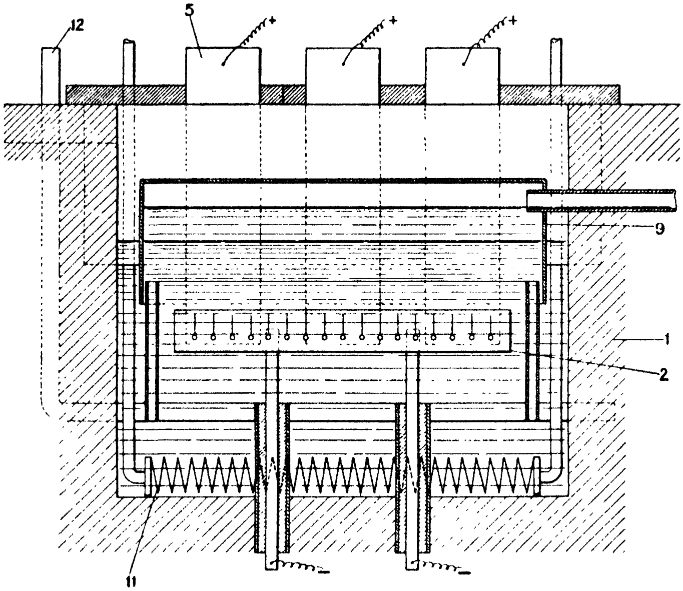


Fig. 19.

1. Fireproof brickwork.
2. Cathode.
3. Cathode conductor.
4. Insulating sleeve.
5. Anode.
6. Diaphragm resistant to chlorine
7. Chlorine ducts.
8. and 10. Diaphragm resistant to sodium.
9. Bell collector for sodium with outlet 13.
11. Resistor heaters.
12. A.C. electrodes.

takes place, or by treating it with native zinc carbonate (calamine) the reaction

$$CaCl_2+ZnCO_3=ZnCl_2+CaCO_3.$$

The filtered solution of zinc chloride is freed from its impurities (amongst which is a not inconsiderable amount of cadmium), and the resultant solution is electrolysed with carbon anodes and circular revolving cathodes that are only partially immersed, to produce chlorine gas and an exceedingly pure metallic zinc. Many of the details are due to C. Höpfner (B.P. 11724, 1894, and D.R.P. 85812, 1895). Fuller details are given in two volumes of "Monographien über angewandte Elektrochemie," xvi., "Die Darstellung des Zinks auf elektrolytischem Wege," Günther, 1904, pp. 99–180, and xxviii. "Die elektrochemische und elektrometallurgische Industrie Grossbritanniens," Kershaw, 1907, p. 108; and also in "Applied Electro-Chemistry," Allmand, 1912, p. 286.

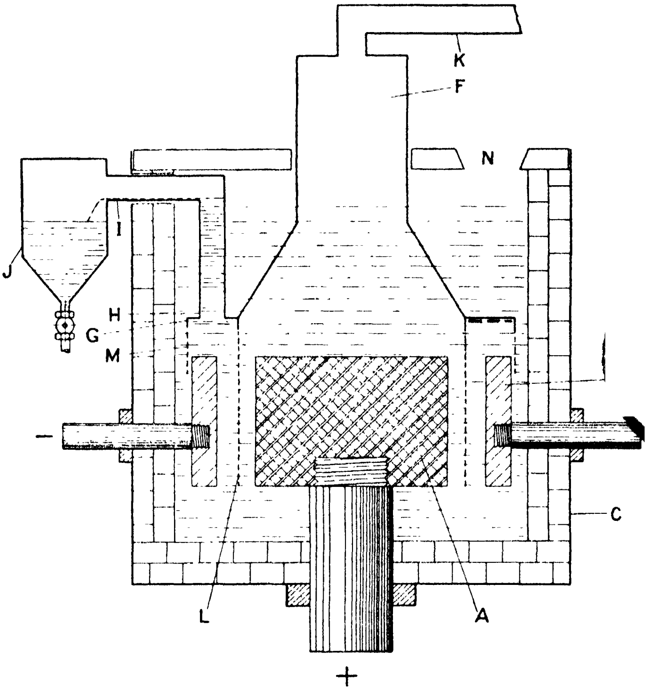


FIG. 20.

A. Anode.
B. Cathode.
C. Cell container.
F. Collector and dome for chlorine.
G. Collector for sodium.
H. Riser pipe for sodium.
I, J. Pipe and receiver for sodium.
K. Chlorine main.
L, M. Diaphragms.
N. Hole in cover for salt charging.

PROPOSALS AND LESS IMPORTANT METHODS FOR THE MANUFACTURE OF CHLORINE.—Many processes have been proposed and tried for utilising the residual ammonium chloride, or the residual calcium chloride of the ammonia soda process, but with the exception of Höpfner's zinc chloride method described above none are now in use. Many other processes have also been tried for preparing chlorine from various sources and in various ways, but have been abandoned. Some of these old methods are enumerated below; fuller information may be obtained from Lunge's "Sulphuric Acid and Alkali," 3rd ed., vol. 3.

1. *Chlorine from Ammonium Chloride.*—The most persistent efforts for the direct manufacture of chlorine from NH_4Cl were made by Mond, who took out B.P. 65, 66, 1049, 3238, of 1886; 10955 and 17273 of 1887; 2160 and 2575 of 1889. Articles dealing with the Mond process are found in J.S.C.I. 1892, 11, 466; 1893, 12, 10, 63. There was also a proposition from the Verein für Chemische Industrie of Mainz (B.P. 3322, 1886).

2. *Chlorine from* $CaCl_2$.—Prolonged efforts for the direct recovery of the chlorine in the $CaCl_2$ produced in the ammonia stills of the ammonia-soda process were made by Solvay: B.P. 77 and 171 of 1877; 838 of 1880; 7258 and 7259 of 1884; 8724 of 1885; 13389 of 1886; 18574 of 1888. Other patents: Twynam's process (B.P. 731 of 1885); Bramley's process (B.P. 8289 of 1887); Lyte and Steinhart (B.P. 21225 of 1890).

Chloride of Lime or Bleaching Powder.—Bleaching powder was first manufactured by Charles Tennant in 1799 at St. Rollox Works, Glasgow, the original patent being B.P. 2312, dated 30 April, 1799. The first year's output was 52 tons and the selling price £140 per ton. During the nineteenth century the production of bleaching powder reached extraordinary tonnages, but for many years now the amount produced has been declining. This is particularly noticeable in North America, where the production at the present time is negligible. In Great Britain the tendency is also marked.

The reasons in the two cases are similar, to the extent that consumers of chlorine in the form of calcium hypochlorite find that technically and economically the production of these solutions from liquid chlorine at the place of use is preferable. In the case of the electrolytic chlorine industry in America, the heat of summer rendered production of bleaching powder a difficult and costly operation, and, in addition, the lack of stability of ordinary bleaching powder in a hot climate caused considerable losses due to deterioration of stocks both at the producing and consuming works.

Composition.—Until 1935 the composition of bleaching powder had not been established in spite of over a hundred years of experimental work, partly on account of the innate complexity of the problem and partly by reason of the differences in samples made in different ways.

From its method of preparation it was originally assumed to be a direct compound of chlorine and lime, hence the name " chloride of lime " ; but in 1835 Balard postulated a compound or mixture of equivalent proportions of calcium hypochlorite and calcium chloride, admixed with calcium hydroxide.

Odling, 1861, without any proof, suggested the constitution $Ca(OCl)Cl$, which was accepted by Lunge, Schappi, and Naef because they found that calcium chloride as such does not exist in bleaching powder, since the substance is not deliquescent nor is calcium chloride extracted from it by alcohol.

Although Kraut (Annalen, 1882, **214**, 354) suggested the existence of a double salt hypochlorite-chloride, the Odling constitution, $Ca(OCl)Cl$, was generally accepted until recent years. The tendency in recent times to discredit the Odling constitution arose from the work of O'Connor, (J.C.S. 1927, 2700), which showed the existence of basic hypochlorites in the calcium hypochlorite–calcium hydroxide–water system.

A most important contribution on this subject has been made by Bunn, Clark and Clifford (Proc. Roy. Soc. 1935, **151**, 141), who attacked the problem by phase rule methods, microscopic examination, and X-ray powder photographs. They showed that the first stage in the reaction is the formation of the basic hypochlorite $Ca(OCl)_2{\cdot}2Ca(OH)_2$, and the basic chloride $CaCl_2{\cdot}Ca(OH)_2{\cdot}H_2O$. On further chlorination the former is converted into another substance which appears to be a mixed crystal the chief constituent of which is calcium hypochlorite.

Ordinary bleaching powder containing about 35% available chlorine is a mixture of this hypochlorite mixed crystal with basic chloride. Further chlorination resulted in partial conversion of the basic chloride into the tetrahydrate $CaCl_2{\cdot}4H_2O$, while the hypochlorite mixed crystal persists.

The non-deliquescent nature of bleaching powder and the difficulty of introducing more than 35–37% available chlorine into the solid are due to the presence of basic chloride, $CaCl_2{\cdot}Ca(OH)_2{\cdot}H_2O$, which appears to be a very stable substance.

These results appear to leave the nature of the hypochlorite mixed crystal as the only substantial problem that has still to be solved.

MANUFACTURE OF BLEACHING POWDER.—Although the production of bleaching powder is rapidly declining, many improvements in the manufacture have been introduced. Attention has been directed to (i) improvement of working conditions and labour saving, (ii) avoidance of corrosion of materials, (iii) production of a drier and therefore more stable product.

Lime.—The quicklime used must be of high grade if a strong bleaching powder is required. Silica should be low, since calcium and magnesium silicates interfere with the settling of bleaching powder solutions. Iron compounds, being catalysts for the decomposition of hypochlorites, are objectionable. Manganese can, under certain conditions, be converted to permanganates and give rise to an undesired purplish colour.

Hand slaking of lime has been entirely superseded by various entirely enclosed mechanical devices which save labour and prevent nuisance from escaping steam and dust.

Although the limestone must be well burned to prevent excess of inert calcium carbonate, a " soft burned " lime is preferred for bleach making. Moreover, since the chlorination is catalysed by water, the slaked lime should contain an excess of " free " water.

Bleaching Powder Chambers.—The traditional lead chamber or Weldon chamber process is now almost if not quite obsolete. The chambers were 10–30 ft. wide, up to 120 ft. long, and with areas up to 3,000 sq. ft. The height was about 6½ ft. to give reasonable head room. The floors were tiles or stone flags; the sides and top were 5 or 6 lb. sheet lead, fastened by external lead straps on an external timber framework. Floor joints were asphalted.

The chambers were preferably erected on pillars, 7–10 ft. high, so that the finished bleach could be packed through trap-doors in the chamber floor. The chambers were fitted with end doors of iron coated with protective paint. " Lutes " were provided for the introduction and removal of gases.

The 3–4 in. layer of slaked lime was spread by shovel and rake. For " gassing," the chambers were worked in series of four or more. The chlorine entered first a nearly finished chamber, and the unabsorbed gas passed in succession through other chambers which were further and further from being finished until the whole of the chlorine was absorbed.

When a chamber was finished, the stream of chlorine was diverted into the next chamber. The residual chlorine in the finished chamber was removed either by dusting in lime by a Brock and Minton's whizzer (B.P. 7199, 1886) or by draughting into a freshly limed chamber. In Great Britain it is illegal to open or vent to atmosphere a chamber containing more than 2½ grains of chlorine per cu. ft. of air.

To overcome difficulties of penetration of the chlorine to the bottom of the lime layer, other systems of gassing were adopted involving the " turning " of the lime by hand at a half-way stage.

100% chlorine cannot be used without dilution, since the heat of reaction causes the temperature to rise higher than 55°, the temperature at which the bleaching powder decomposes vigorously. On the other hand, Weldon chambers are not very suitable for the absorption of extremely dilute chlorine. This would involve a disproportionately small output. Worked under the best conditions the output may be reckoned as 2–2½ lb. of bleaching powder per square foot of area per day (Lunge's " Sulphuric Acid and Alkali," 3rd ed., vol. 3, p. 618 ; 21st Report of Chief Inspector of Alkali Works for the year 1884).

Various plant have been devised either to absorb dilute chlorine or to improve working conditions.

Deacon chlorine because of its low strength was absorbed in a shelf chamber plant, Fig. 21, consisting of staggered shelves which formed a zig-zag path for the gases. A shallow layer of lime was raked on each shelf, the lime being fed through holes in the shelves which were successively covered with plates as the shelves were charged from the lowest upwards.

The Hasenclever plant (B.P. 17012, 1888), shown in Figs. 22 and 23, consisted of several superimposed iron cylinders fitted with central shafts carrying blades. The shafts were driven by geared wheels coupled together and the set of the blades caused the lime fed at the gas outlet of the top cylinder to travel countercurrent to the ascending dilute chlorine. This plant, designed for Deacon chlorine, was used for diluted electrolytic chlorine, but like the Deacon chambers has been largely displaced by the following mechanical plant.

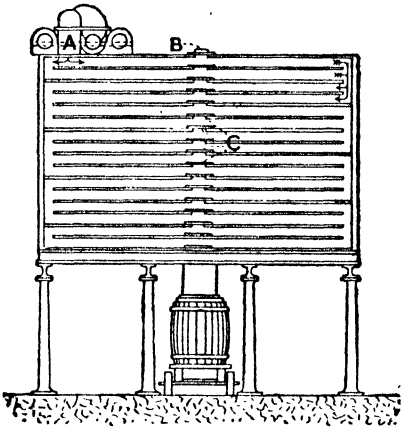


Fig. 21.

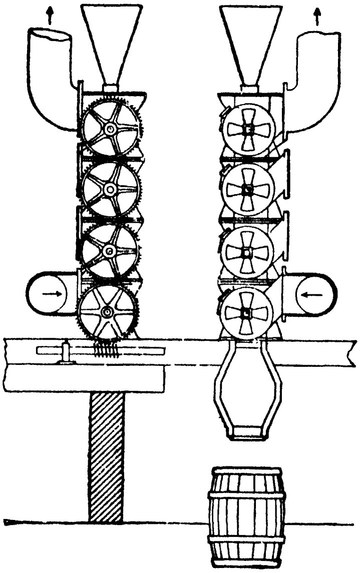


Fig. 22.

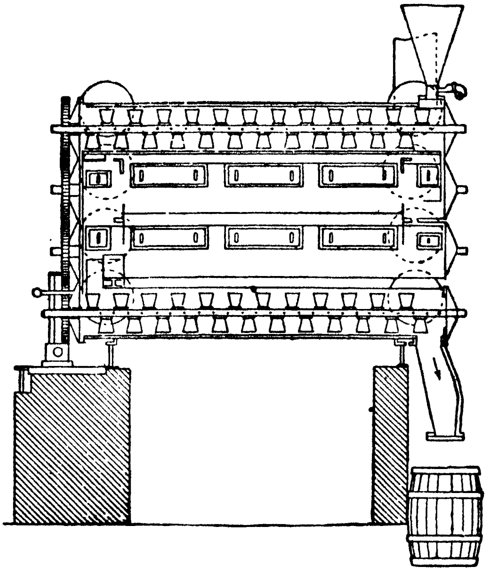


Fig. 23.

Backman Chambers.—This apparatus invented by Nils Backman (G.P. 404768, 1922; 435019, 1925; 451114, 1926) consists of a number (usually eight) of superimposed substantially circular chambers, on the floors of which the descending lime and bleach are made to travel alternately from the centre of the floor to the rim and from the rim to the centre, by means of ploughs on rotating arms, in counter current to a stream of chlorine. The chamber is constructed of concrete and independent cooling coils are embedded in the concrete floors. The product by this means can be kept at a temperature below 40°C.

Moore Tube.—The Moore rotary tube (B.P. 113457, 1916, Moore and Castner-Kellner Alkali Co., Ltd.) is described as a rotating cylinder not much shorter than 80 ft. long, preferably with a suitable fall, and lined with tiles or other suitable material, through which lime travels counter-current to chlorine. Advantages claimed are the absence from the bleaching powder of products of corrosion of iron which cause instability, and reduced maintenance costs.

Rudge Tube.—The Rudge rotary tube (B.P. 126773, 1918, Rudge and United Alkali Co., Ltd.) is described as a rotatable cylinder, usually 60 ft. long, carried horizontally on rollers and fitted with lifters which cause the lime to travel in counter current to chlorine gas. The cylinder is made of mild steel and can be cooled by an external water spray where required. Also a circulatory system is adopted for the chlorine gas with permissive external cooling (*see also* Nydegger, G.P. 370841, 1920).

Stable Bleaching Powder.—The keeping properties (stability) of bleaching powder have been the object of study since 1874. In recent years more attention has been paid to this problem with the object of producing a stable product.

In J.S.C.I. 1918, **37**, 311T, an article by Rettie, Lorrain Smith and Ritchie describes tests with bleaching powder to which quicklime had been added in order to reduce by its slaking the free water and water of crystallisation of bleaching powder. The product was of lower available chlorine content but was remarkable for its stability (*see also* J.S.C.I. 1921, **40**, 240T; B.P. 242805, 1924, Lamble and United Alkali Co., Ltd. ; B.P. 349358, 1930).

In 1925 Conroy, Lamble, Latham and United Alkali Co., Ltd., devised a process for the production of dry and, therefore, stable bleaching powder (B.P. 246000). Further technical improvements in the production of dry bleaching powder are described in B.P. 317572, Moore, Lamble, and I.C.I., Ltd., 1928; and B.P. 344012, Carter and I.C.I., Ltd., 1929.

Stable bleaching powder is particularly desired for use in tropical countries, which has resulted in the product becoming known in the trade as " Tropical " bleach. A novel process by Carrughi and Paolini of Societa Elettrica ed Elettrochimica del Caffaro for the production of dry bleaching powder is described in B.P. 317716, 1928; 362068, 1930; and 365019, 1931, according to which hydrated lime in suspension in carbon tetrachloride is chlorinated and the solvent removed by distillation, which removes the water at the same time. The product is known as " Sichlor " (*see also* Chem. Met. Eng. 1932, **39**, 140; B.P. 357933, I.G. Farbenfabriken).

The effect of heating bleaching powder is discussed by Ditz (Z. Angew. Chem. 1901, **14**, 3, 25, 49, 105).

The following table gives the composition calculated from analyses of various types of bleaching powder. Under the heading " Heat Test," are given the results of heating samples in test tubes to 100°C. for 2 hours, a convenient method of comparison of the stability of bleaching powders.

	Chlorine.		$CaOCl_2$	$CaCl_2$	$Ca(ClO_3)_2$	$Ca(OH)_2$	$CaCO_3$	H_2O	Avail. Cl_2 after heat test.
	Available.	Total.							
Chamber bleach . . .	39·58	40·10	70·79	0·78	0·15	11·62	2·30	13·04	14·94
Hasenclever bleach . .	36·20	37·90	64·80	2·46	0·34	22·98	3·43	4·99	—
Moore rotary bleach . .	36·85	39·26	65·93	3·36	0·75	21·66	1·30	5·95	—
Rudge rotary bleach . .	35·75	37·30	63·98	2·30	0·24	22·80	2·85	6·43	26·81
Backman bleach . . .	38·20	38·90	68·38	1·09	0·10	16·58	3·60	9·56	—
Tropical bleach . . .	35·85	39·36	64·13	5·08	0·75	26·53	1·30	1·16	32·75
Caffaro bleach . . .	37·50	38·97	67·11	2·19	0·20	26·48	1·00	1·84	33·00

Bleaching Powder: Heat of Formation.—Results expressed as cals. per kg. of available chlorine.

O. Nydegger (Chem. Met. Eng. 1923, **30**, 1141), 265,000 cals.

Neumann and Müller (Z. angew. Chem. 1925, **38**, 194), 247,000 cals.

Neumann and Hauck (Z. Elektrochem. 1926, **32**, 27), 252,000 cals.

The nature of the determination of these authorities was such that little or no water was evaporated, but no record of the free water content of the bleach was given.

Bleach Liquor.—Bleach liquor is produced in chlorine works for delivery within a circumscribed area. It is also made by solution of bleaching powder in water; the large amount of sludge remaining may, however, cause difficulty in disposal. The amount of sludge may be reduced by chlorination of the free lime, liquid chlorine being used for the purpose. As a further step, milk of lime may be directly chlorinated. Since 1918, when liquid chlorine has become generally available in Great Britain, these later processes tend more and more to be adopted, proving more economical. During the preparation of bleach liquor decomposition occurs if the temperature exceeds 40°C. Evaporation of liquid chlorine is utilised for cooling by direct introduction of the liquid into milk of lime in cast-iron vessels. In order to obtain complete absorption of chlorine in milk of lime a peripheral speed of 500 ft. per min. for the agitation is desirable, and the depth of the chlorinator will depend on the quantity of gas to be absorbed in unit time.

A convenient method for the preparation of bleach liquors on a small scale (batches of 70 lb. chlorine) is by the use of the Golding-Pritchard chlorinator (B.P. 233490). The chlorine valve is automatically controlled by progress of the chlorination, which causes the rise or fall of a gas bell.

In addition to the use of bleach liquor for bleaching cellulose, it is used for the removal of oxidisable sulphur bodies from the lighter fractions of mineral oil.

Analysis of Bleach Liquors and Allied Products.—The best method for the determination of available chlorine is due to Penot. A suitable measured quantity of bleach liquor or other solution of hypochlorite is titrated with sodium arsenite solution in the presence of an excess of sodium bicarbonate, the end point being determined by spotting, using starch iodide as an indicator.

The alkalinity of hypochlorite solutions is most conveniently determined by titration of the solution with acid, using phenolphthalein and methyl orange as indicators, subsequent to destruction of the hypochlorite by means of an excess of neutral hydrogen peroxide:

$$Ca(OCl)_2+2H_2O_2=CaCl_2+2H_2O+2O_2$$

An apparatus for the rapid determination of available chlorine in weak hypochlorite liquor is described by J. M. Taylor, Ind. Chem. 1929, *5*, 135.

Calcium Hypochlorite, $Ca(OCl)_2$.—Crystalline calcium hypochlorite was first prepared by Kingzett (J.C.S. 1875, **28**, 404; Chem. News, 1875, **32**, 22; 1882, **46**, 120) by evaporation or freezing of bleaching powder solutions (*see also* Orton and Jones, J.C.S. 1909, **95**, 751; Proc. Chem. Soc. 1909, **25**, 74). It crystallises from water in minute needles with 3 mols. of water of crystallisation (Urano, Trans. Electrochem. Soc. 1926, **49**, 65; O'Connor, J.C.S. 1927, 2700). The solubility of calcium hypochlorite in water at 0°C. is 21·8%. With hydrated lime calcium hypochlorite forms basic hypochlorites, $Ca(OCl_2)\cdot 3Ca(OH)_2$ and $Ca(OCl)_2\cdot 2Ca(OH)_2$, which are less soluble than calcium hypochlorite. *See* O'Connor (*l.c.*), who studied the system

$$Ca(OCl)_2/Ca(OH)_2.$$

The available chlorine content of bleaching powder (35–37% commercial standard) compares very unfavourably with pure calcium hypochlorite (99·2%).

Since 1906 the large number of patents and the very appreciable volume of work indicate the interest of the chemical industry in the production of pure calcium hypochlorite. The successful exploitation of this work is due chiefly to Chemische Fabrik Griesheim-Elektron, I G., who market a product known as "Perchloron," which contains approximately 75% available chlorine. Griesheim-Elektron, (G.P. 188524, 1906, and B.P. 8476, 1907), describe the chlorination of milk of lime nearly to saturation and concentration of the filtrate *in vacuo*. Crystals of calcium hypochlorite hydrate separate out, are filtered, and then dried *in vacuo* (*see also* B.P. 17859, 1914, and G.P. 282746, 1913). The product is said to contain 80–90% available chlorine and to be more stable than bleaching powder.

Mathieson Alkali Works Inc. market a product H.T.H. (High Test Hypochlorite) which contains upward of 60% available chlorine (Gage, Chem. Met. Eng. 1929, **36**, 295).

In B.P. 317233, 1928 (Mathieson Alkali Works Inc.), it is stated that calcium hypochlorite in pure form is relatively stable, but the presence of calcium chloride in substantial amount makes it relatively unstable, owing to the hygroscopic properties of the salt.

The low solubility of basic calcium hypochlorite may be used in the production of calcium hypochlorite to remove calcium chloride from the product at an intermediate stage:

$$(1)\quad 5Ca(OH)_2+2Cl_2 = Ca(OCl)_2\cdot 3Ca(OH)_2+CaCl_2+2H_2O$$

$$(2)\quad 2[Ca(OCl)_2\cdot 3Ca(OH)_2]+6Cl_2 = 5Ca(OCl)_2+3CaCl_2+6H_2O$$

The preparation of basic calcium hypochlorite is described in G.P. 195896, 1907, and 373847, 1921, B.P. 182927, 1921, and 188662, 1922, of Griesheim-Elektron; and its isolation by centrifuging is described in G.P. 451665, 1926, B.P. 276307, 1927, also of Griesheim-Elektron. A product containing approximately 40% available chlorine and 5–15% of water is obtained.

Dry basic hypochlorite has been sold under the name of "Basogrelit." The chlorination of basic calcium hypochlorite in aqueous suspension yields calcium hypochlorite which separates out under suitable conditions in crystalline form (G.P. 195896, 1907; F.P. 370863, 1906; U.S.P. 934467, 1906; and B.P. 24101, 1906). Urano and Imai (B.P. 266180, 1926) describe the production of basic calcium hypochlorite by the addition of the requisite quantity of lime to a clear solution of bleaching powder and concentration *in vacuo*. In B.P. 266181, 1926, the same inventors treated the basic salt obtained according to the previous patent with water, filtered off the lime and obtained calcium hypochlorite by concentration *in vacuo*. The dried product contained 90–99% available chlorine.

F. N. Kitchen and I.C.I., Ltd. (B.P. 378847, 1931), and F. T. Meehan, F. N. Kitchen, and I.C.I., Ltd. (B.P. 404627, 1932) describe cyclic processes for the production of normal calcium hypochlorite by separation of either monobasic calcium hypochlorite or dibasic calcium hypochlorite as an intermediate stage. The mother liquor is rejected. The separated basic calcium hypochlorite is subsequently chlorinated in the presence of additional water to produce solid normal calcium hypochlorite. The mother liquor separated from the crystals of normal calcium hypochlorite is recirculated to the first stage in the process, where it is mixed with additional lime slurry. The dried product contains 75% or more available chlorine.

A series of patents by Mathieson Alkali Works Inc. describes the production of calcium hypochlorite by neutralisation of hypochlorous acid with milk of lime. Hypochlorous acid is produced by chlorination of a suspension of calcium carbonate. The aqueous solution is extracted with carbon tetrachloride (containing 2% alcohol) or amyl alcohol (U.S.P. 1481039, 1924; U.S.P. 1481040, 1924; U.S.P. 1632483, 1927; B.P. 195366, 1923; B.P. 216450, 1923). The chlorine may be removed as a solid organic derivative such as acetochloroanilide, which reacts slowly with water to give hypochlorous acid (U.S.P. 1609328, 1926).

Mathieson Alkali Works Inc. has a series of patents for the production of calcium hypochlorite which are based on the addition of alkali either as caustic soda or sodium hypochlorite to lime or chlorinated lime suspensions. In this way calcium chloride is replaced by sodium chloride, which results in easier removal and purification of the solid phase:

$$2Ca(OH)_2+2Cl_2=Ca(OCl)_2+CaCl_2+2H_2O$$
$$CaCl_2+2NaOH=Ca(OH)_2+2NaCl$$
$$CaCl_2+2NaOCl=Ca(OCl)_2+2NaCl$$

The solid phase consists essentially of calcium hypochlorite hydrate and sodium chloride, and a product of high available chlorine content can be obtained, which is presumably dried *in vacuo* (G.P. 473924, 473925, 473975, 473976, 474080, 474220, 477383; B.P. 314447, 321250, 321720, 323205; 1927–1928).

An analysis of the Mathieson product is:

	%
Available chlorine . .	63·0
$CaCl_2$	0·5
Free lime	3·5
Inert constituents . .	31·5
Water	1·5

(Gage, Chem. Met. Eng. 1929, **36**, 295).

The production of a triple salt,

$$Ca(OCl)_2,NaOCl,NaCl,12H_2O,$$

by the addition of sodium chloride to a solution made by chlorination of lime is described in B.P. 317437, 319727, 320182, 1927, of Mathieson Alkali Works Inc.

The use of caustic soda to displace some of the lime used in the process of manufacture of calcium hypochlorite would appear to result in an increased cost of manufacture.

The obvious difficulties in the manufacture of calcium hypochlorite are:

(1) The chlorination of a cream of lime. A cream of lime which is fairly fluid becomes thicker as the formation of basic calcium hypochlorite takes place until it has the consistency of porridge. Further chlorination to calcium hypochlorite causes an increase in fluidity. Great care is essential if decomposition of hypochlorite to chlorate is to be avoided.

(2) Calcium hypochlorite hydrate in the form of fine needles must be freed from a fairly concentrated solution of calcium chloride if a high-test final product is to be obtained. The operation presents considerable difficulty.

(3) The materials of construction of the plant must be selected to prevent the product becoming contaminated with catalytic bodies which would cause decomposition, *e.g.* salts of iron, nickel, etc.

(4) Drying of the filter cake must be carried out at low temperature, otherwise decomposition similar to that of bleaching powder on heating will take place (Ditz, Z. angew. Chem. 1901, **14**, 3, 25, 49, 105).

"Maxoclor," a calcium hypochlorite product containing 75% or more of available chlorine, is manufactured in England by Imperial Chemical Industries, Ltd. "Perchloron" is manufactured in U.S.A. by Pennsylvania Salt Co. at Wyandotte (Chem.-Ztg., Oct. 1931, 780).

Manufacture of calcium hypochlorite is carried out in Japan by Kojimachi-Ku Co. (World Trade Notes on Chemicals, Feb. 1931, p. 2).

Potassium Hypochlorite Solution (Chloride of Potash or Eau de Javelle).—This liquor was first made in 1789 at the Javel Works near Paris, and was the first bleaching compound known. It was then made by passing chlorine into a solution of potashes (crude potassium carbonate) in eight parts of water. It is no longer used, having been replaced by the cheaper sodium and calcium hypochlorites.

Sodium Hypochlorite Solution (Eau de Labarraque, usually called Eau de Javelle).—As originally prepared, by passing chlorine into a solution of sodium carbonate until the liquid began to effervesce, sodium hypochlorite solution was very unstable. This high instability was caused by the presence of substantial amounts of hypochlorous acid, which is a weaker acid than carbonic acid.

Hypochlorite of soda solution is now prepared by one of the three following processes:

1. By double decomposition of calcium hypochlorite and sodium carbonate or sulphate with precipitation of the calcium as carbonate or sulphate:

$$Ca(OCl)_2+CaCl_2+2Na_2CO_3$$
$$=2CaCO_3+2NaOCl+2NaCl$$

The calcium hypochlorite may be as bleaching powder or as one of the modern "high-strength" calcium hypochlorites. This method is usually adopted for bleaching purposes in smaller factories.

2. By passing chlorine into a solution of caustic soda until nearly all the soda is chlorinated:

$$Cl_2+2NaOH=NaOCl+NaCl+H_2O$$

Substantial amounts of this solution are made at electrolytic alkali works, and sold at strengths of 10–15% available chlorine. Sodium hypochlorite may, however, be conveniently prepared *in situ* from sodium hydroxide solution and liquid chlorine.

It has been found necessary to leave a small amount of free sodium hydroxide, say 0·3%, in order to make the solution stable.

3. By electrolysis of brine solution. Under Production of Chlorine, electrolytic cells devised to liberate chlorine from common salt solution have been discussed. In the case of the preparation of sodium hypochlorite there is no necessity

when the electrolysis starts to keep the main products, chlorine and caustic soda, apart; indeed, they must be brought together. This contravenes the generalisation that the products of electrolysis must be kept separate in the cell and, consequently, a sodium hypochlorite cell compares very unfavourably with the chlorine cell with subsequent recombination of chlorine and caustic soda outside the cell.

As in chlorine cells (excluding those with mercury cathodes) the primary products of the electrolysis are hydrogen and caustic soda at the cathode, and chlorine at the anode. With the mixing of catholyte and anolyte, sodium hypochlorite is formed:

$$Cl_2 + 2OH' = Cl' + OCl' + H_2O$$

or $Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$.

Since sodium chloride is reformed, the net reaction

$$NaCl + H_2O = NaOCl + H_2$$

is the result of the passage of two faradays. A number of side reactions are important. Since, in spite of mixing, there will be an excess of chlorine near the anode, sodium chlorate will be formed chemically:

$$2HClO + ClO' = ClO_3' + 2Cl' + 2H^{\cdot};$$

but, at ordinary working temperatures, this reaction is slow and unimportant. Electrolytic reactions are more important. At the cathode, hypochlorite is reduced by the nascent hydrogen:

$$ClO' + 2H^{\cdot} = Cl' + H_2O$$

The effects of this reaction may be lessened by the addition of potassium chromate, a vanadium salt, sodium resinate, or Turkey red oil in presence of calcium salts. These agents appear to yield a thin porous diaphragm round the cathode and so prevent the bulk of the solution from coming into contact with the active hydrogen.

If the hypochlorite ion concentration in the anode layer becomes appreciable hypochlorite ions will be released. According to Foerster and Müller (Z. Elektrochem. 1902, **8**, 665), the net reaction is:

$$6ClO' + 3H_2O = 6H^{\cdot} + 2ClO_3' + 4Cl' + 1\tfrac{1}{2}O_2 + 6e$$

This reaction limits the hypochlorite concentration attainable, although loss may be minimised, at the expense of the lesser evil of chemical formation of chlorate, by not mixing efficiently in the immediate neighbourhood of the anode. Moreover, since the ratio of chloride to hypochlorite must be kept high, a large consumption of salt is necessary.

Allmand and Ellingham ("Applied Electro-Chemistry," London, 1924, p. 375) summarise the most favourable conditions for the electrochemical production of hypochlorite solutions as:

(1) An electrode arrangement which will permit of an undisturbed diffusion layer being formed at the anode.

(2) A neutral electrolyte.

(3) Strong NaCl solution, both to lower the resistance and to permit the production of stronger hypochlorite solutions.

(4) Low temperature.

(5) High anodic current density.

(6) Presence of potassium chromate.

(7) Use of platinised platinum electrodes.

In spite of the very formidable difficulties, several technical cells have been developed for use in districts where sodium hypochlorite or liquid chlorine is not readily available.

Kellner Cell: Vertical Type (Fig. 24).—This cell, now obsolete, consisted of a stoneware vessel divided into a number of small compartments by glass plates fitting into small grooves in its sides. The glass plates were wound with platinum-iridium wire, which formed bipolar electrodes. The electrolyte was circulated rapidly through the cell and a cooling coil.

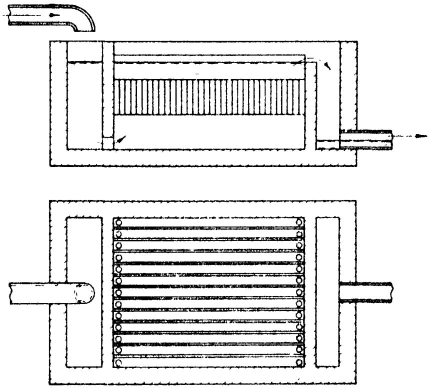


Fig. 24.

The Haas-Oettel Cell consists of a rectangular box divided into small compartments by a series of vertical bipolar graphite electrodes set in grooves. The electrolyser stands in a tank of brine and circulation is effected automatically by the gas evolution.

The Schuckert Cell is a large stoneware trough divided into 8 to 10 compartments by means of vertical glass plates. The bipolar electrodes may be all carbon or half may be carbon and the other half platinum-iridium foil. Circulation is by means of the hydrogen evolved and is through all compartments in series, thus differing from the Kellner vertical and Haas-Oettel cells, where several passages through one compartment are obtained. Some types of Schuckert cell are provided with alternate cooling compartments.

Kellner Cell: Horizontal Type (G.P. 165486, 1902).—This cell consists of a long concrete trough divided into compartments by vertical plates of glass. The compartments are arranged as a cascade and the horizontal electrodes of platinum-iridium are bipolar, acting as cathode in one compartment and as anode in the next. The electrodes pass beneath the glass divisions and the cathode is above the anode. The electrolyte flows by gravity through all the compartments in series (Fig. 25).

Comparison of Cells.—The following table is based on figures given by Allmand and Ellingham (*op. cit.*) -

Type.	Grams avail. Cl_2 per litre.	kw. hrs. per ton of avail. Cl_2.	Tons of salt per ton of avail. Cl_2.
Kellner (vertical)	12	6,600	12·5
Haas-Oettel . .	12·3	6,500	14
Schuckert . . .	20	6,100	7·5
Kellner (horizontal)	25	6,100	6

It will be seen that normally these cells cannot compete with sodium hypochlorite or liquid chlorine produced by an alkali works.

For further details, *see* Allmand and Ellingham (*op. cit.*) ; or the article " Hypochlorite und elektrische Bleiche," by Billiter and Fuchs, in Vol. 2, part 2, of Engelhardt's " Handbuch der technischen Elektrochemie " ; Kurt Arndt, " Technische Elektrochemie."

Uses of Sodium Hypochlorite Solutions.—The chief use of sodium hypochlorite solution is the bleaching of high quality fabrics made from vegetable fibres. It is also used in laundries. Sodium hypochlorite solution possesses strong germicidal powers and is used very extensively as a disinfectant. It is also used in the production of unshrinkable woollen goods.

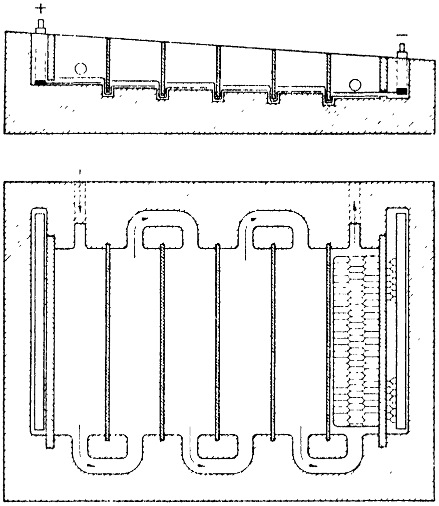


FIG. 25.

Chlorates.—The chlorination of hot alkali solutions gives a mixture of chloride and chlorate in the molecular ratio of 5 to 1, according to the equation :

$$6KOH+3Cl_2=5KCl+KClO_3+3H_2O$$

This contrasts with the reaction in the cold to give hypochlorite :

$$2KOH+Cl_2=KClO+KCl+H_2O\ ;$$

but heating the hypochlorite solution after neutralisation of the residual alkalinity causes decomposition to chlorate. Empirically the reaction may be written

$$3KClO=KClO_3+2KCl,$$

but the actual mechanism is possibly very complex.

MANUFACTURE OF CHLORATES.—1. CHEMICAL METHODS.—Originally potassium chlorate was manufactured by chlorination of potassium hydroxide solution, but this process was abandoned owing to the conversion of over five-sixths of the expensive potassium into relatively useless potassium chloride. A suggestion of Liebig led to the adoption of a process depending on the chlorination of milk of lime to calcium chlorate and calcium chloride,

$$6Ca(OH)_2+6Cl_2 \\ =3Ca(OCl)_2+3CaCl_2+6H_2O,$$

$$3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2,$$

followed by double decomposition of the calcium chlorate with potassium chloride to give potassium chlorate :

$$Ca(ClO_3)_2+2KCl=CaCl_2+2KClO_3$$

Since calcium chlorate, calcium chloride, and potassium chloride are all very soluble in water, and potassium chlorate is only sparingly soluble, the reaction could be carried out with little loss of potassium chloride.

The first stage, the preparation of calcium hypochlorite solution, was carried out in cast-iron vessels. The temperature was kept below 35°C. to decrease the decomposition of the hypochlorite to chloride and oxygen,

$$Ca(OCl)_2=CaCl_2+O_2,$$

a reaction catalysed by iron salts.

When all the lime was neutralised spontaneous decomposition to chlorate took place with considerable rise in temperature. The crude solution of calcium chlorate and calcium chloride was concentrated and settled or filtered. After addition of a slight excess of potassium chloride solution, the solution was once more concentrated, settled, and the clear solution cooled. The crude potassium chlorate was purified by recrystallisation.

Two important variations of this process were worked out. In the Péchiney process the original solution of calcium chlorate and calcium chloride was concentrated until a considerable amount of the calcium chloride had crystallised out (probably as $CaCl_2,6H_2O$). In this way the amount of calcium chloride remaining in solution could be reduced to a molecular ratio $CaCl_2 : Ca(ClO_3)_2$ of 1·2 : 1. There was, therefore, a greatly decreased bulk of calcium chloride solution with consequent decreased losses of potassium salts in the mother liquors.

In the Muspratt process magnesia was used instead of lime. The molecular ratio of chloride to chlorate was only about 5·1 : 1, as against 5·3 : 1 for the lime process. The liquor was evaporated and magnesium chloride hexahydrate crystallised out until the molecular ratio of chloride to chlorate in the solution fell to 2·8 : 1. After double decomposition of the magnesium chlorate with potassium chloride and crystallisation of the potassium chlorate, magnesium chloride was recovered from the mother liquors. This process had two serious disadvantages :

(1) The magnesium chloride could not be sold profitably.

(2) Magnesium chloride solutions are very corrosive.

Sodium Chlorate.—Owing to the great solubility of sodium chlorate, manufacture by chemical methods presented considerable difficulties.

Péchiney Process.—The chlorate-rich solution obtained in the Péchiney process for potassium chlorate was treated with solutions of sodium sulphate, precipitating all the calcium as calcium sulphate. The solution of sodium chloride and sodium chlorate was concentrated by evaporation with separation of most of the sodium chloride. The solubility of sodium chlorate increases rapidly with increasing temperature, but the solubility of sodium chloride increases little. Cooling of the chlorate-rich solution, therefore, yielded sodium chlorate containing relatively little sodium chloride.

Muspratt Process (*see above*).—The liquors, containing magnesium chlorate and reduced amounts of magnesium chloride, obtained as in the process for potassium chlorate, were treated with sodium carbonate to precipitate all the magnesium as basic magnesium carbonate, which was used to prepare magnesia for the initial chlorination. The solution of sodium chloride and sodium chlorate was worked up as in the Péchiney process.

The chemical methods for the manufacture of chlorates have been superseded by the electrochemical methods.

2. ELECTROCHEMICAL METHODS. — Under sodium hypochlorite (*q.v.*) it has been shown that chlorate may be formed electrochemically by the reaction:

$$6ClO' + 3H_2O = 6H^{\cdot} + 2ClO_3' + 4Cl' + 1\tfrac{1}{2}O_2 + 6e \quad \text{(i)}$$

or chemically by the reaction:

$$2HClO + ClO' = ClO_3' + 2Cl' + 2H^{\cdot} \quad \text{(ii)}$$

These two reactions are the basic reactions in the two types of cell which have been developed for the production of chlorates.

(i) *Electrolysis of Alkaline Alkali Chloride Solutions.*—Consideration of the reaction (i) above with the necessary previous reactions,

$$12Cl' = 6Cl_2 + 12e.$$

$$6Cl_2 + 6OH' = 6ClO' + 6Cl' + 6H^{\cdot},$$

shows that, since hypochlorite is both formed and decomposed by electrochemical reactions, the formation of 6 gram-ions of chlorate is the result of the passage of eighteen faradays, of which twelve are used to produce active oxygen in the form of chlorate and six yield gaseous oxygen. The maximum current efficiency is, therefore, 66·7%. Moreover, since hypochlorous acid is an extremely weak acid and a maximum concentration of hypochlorite ions at the anode is desirable, the alkali chloride solution must be alkaline. If the alkalinity is excessive, trouble is experienced owing to the direct discharge of hydroxyl ions at the anode.

Gall and de Montlaur (B.P. 4686, 1887) described a process for the production of alkali chlorates. A stoneware trough was divided by a porous asbestos diaphragm. The cathodes were made of iron, or preferably nickel; the anodes were of platinum-iridium foil. The current density was 50 amps. per square decimeter, and the voltage 4·5 to 5·0.

Although, according to Billiter ("Techn. Elektrochemie," II, 358), the current efficiency was only of the order of 25%, this process had considerable commercial success owing to its simplicity and the availability of very cheap power.

Hurter (B.P. 15396, 1893) also described a cell for the production of potassium chlorate by the electrolysis of alkaline potassium chloride solutions.

These processes have now been completely superseded by processes involving the electrolysis of acidic alkali chloride solutions.

(ii) *Electrolysis of Acidic Alkali Chloride Solutions.*—The basic reaction of the production of chlorates by the electrolysis of acid solutions of alkali chlorides is shown by equation (ii) above.

This reaction proceeds extremely slowly in alkaline solution owing to the neutralisation of the hypochlorous acid. Hypochlorous acid, is, however, a very weak acid, and the formation of chlorate may be considerably accelerated by making the solution weakly acidic. Moreover, the temperature coefficient of the velocity of reaction is high, so that increase in temperature causes a very great increase in the rate of formation of chlorate. Since formation of chlorate by the discharge of hypochlorite ions is disadvantageous (wasting energy), it is desirable to have a large volume of electrolyte compared with electrode area or total current, as the chemical formation of chlorate proceeds throughout the electrolyte, and is not restricted to the neighbourhood of the electrodes. Cathodic reduction is best avoided by the addition of a small amount of potassium chromate.

Originally platinum or platinum alloys were extensively used as anodes. Graphite is rapidly attacked at the high temperatures (80°–90°C.) originally employed, but the very great fluctuations in the price of platinum have led to the use of graphite at relatively low temperatures (40°C.).

1. *Barker Cell.*—In the cell developed by J. T. Barker for the United Alkali Co., the container is a narrow iron trough, the lower part being covered with cement. The cathode consists of the exposed part of the iron trough and a central iron cooling coil. The anodes are vertical, cylindrical graphite rods. To decrease oxidation of the anodes, the graphite is impregnated with paraffin wax or other inert organic material. The cell top is a plate of an asbestos composition and the anodes are supported by ebonite rods passing through the tops of the graphite and resting across the top of the trough.

A 1,500-amp. cell is about 8 ft. long, 4 ft. deep, and 8 in. wide. The working temperature is about 40°C (Fig. 26).

2. *Aussiger Verein Cell.*—In this cell special attention has been paid to the use of a large volume of electrolyte for a given electrode area, so that the chemical production of chlorate may be accelerated while electrolytic discharge of hypochlorite ions is hindered. Only the lowest

quarter of the concrete trough is occupied by the electrodes which consist of alternate graphite slab anodes and iron strip cathodes. All the anodes are connected to a graphite block, from which a graphite rod rises to above the electrolyte. The cathode connection is an iron bar passing through the side of the cell to which the individual cathodes are fastened.

3. *Angel Cell.*—In this cell also the volume of electrolyte is large, but the electrodes are suspended at the top of the cell with the space for the chemical reaction at the bottom. Graphite anodes and iron cathodes are used, and a special feature of the cell is the setting of the cathodes relevant to the anodes. If the electrodes are set parallel, their resistance causes most of the current to pass between the tops of the electrodes, with consequent rapid destruction of the tops of the graphite anodes. In the Angel cell, therefore, the iron cathodes are set at an angle so that the distance from the anode is greater at the top of the electrode than at the bottom. This gives more even wear and longer life of the anodes.

The cell container is either iron or lead-covered iron. The temperature is maintained at 40°–50°C. by circulation of the electrolyte.

Safety Precautions in the Manufacture and Use of Chlorates.—Owing to the very high proportion of available oxygen, chlorates are dangerous in contact with combustible materials. In Great Britain special washed clothing must be provided for every worker engaged in crystallising or grinding chlorates. The use of wooden vessels for crystallising potassium chlorate has in the past led to disastrous fires and explosions.

Uses of Chlorates.—Chlorates have been used in the manufacture of matches and explosives and in the development of dyes. A recently developed use is that of sodium chlorate as a relatively non-toxic weed-killer, but a disadvantage is the risk of fire when wood or other combustible material is left in contact with these substances.

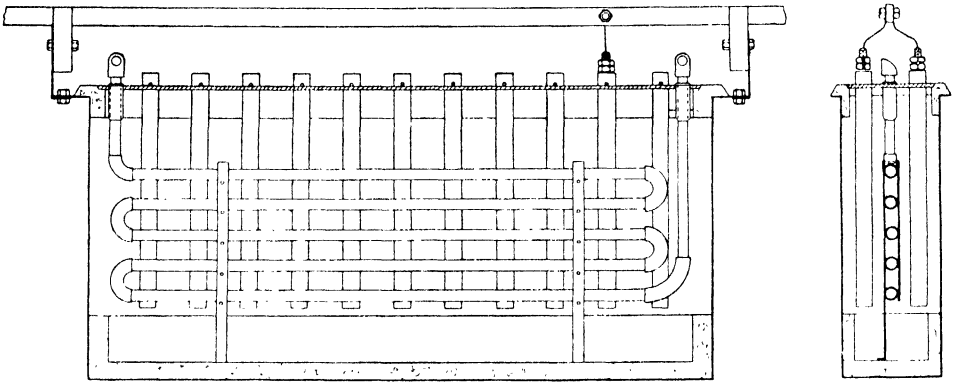


FIG. 26.

Perchlorates.—Although potassium and ammonium perchlorates are technically more important than the hygroscopic sodium perchlorate, sodium chlorate is the usual raw material since its great solubility is advantageous for the electrolytic preparation of sodium perchlorate. Although the empirical sum of the cell reactions may be written

$$NaClO_3+H_2O=NaClO_4+H_2,$$

the actual mechanism of the reactions is very complex, chlorites being probably formed as an intermediate, while chlorides are inevitable by-products of the reactions. The mechanism of this formation has been represented as the result of:

(i) cathodic reduction of chlorate,

(ii) chemical decomposition of chlorate,

$$4NaClO_3=3NaClO_4+NaCl,$$

(iii) the reactions

$$2HClO_2=HClO_3+HClO$$
$$3HClO=HClO_3+2HCl$$

The second of these possibilities is probably quite unimportant.

As electrolyte a concentrated solution (60–70%) of sodium chlorate is used. The cathodes are iron and the anodes smooth platinum. A very high anode potential is essential and, therefore, graphite and magnetite are unsuitable. Normal cathode current densities of 10–20 amps. per square decimetre are used, but the anode current densities are extremely high, ranging from 30 to 70 amps. per square decimetre. Originally low temperatures were used, but modern practice allows temperatures as high as 60°C.

The discharge of perchlorate ions, with consequent release of oxygen and drop in current efficiency, is not serious until very high perchlorate-chlorate ion ratios are reached. This fact is important, since potassium perchlorate and potassium chlorate form mixed crystals, and a very high sodium perchlorate-sodium chlorate ratio must, therefore, be obtained in the electrolytic cell.

In practice, current efficiencies are about 80–90%.

Perchlorates are used extensively in some types of explosives. In recent years perchloric acid has been used as an important analytical reagent (*v.* CHEMICAL ANALYSIS, Vol. II, p. 584*d*), and magnesium perchlorate) *anhydrone*) as a drying agent in analysis.

Bibliography.—Allmand and Ellingham, "Applied Electrochemistry," 1924; "Handbuch der technischen Elektrochemie," vol. 2, part 2, edited by Engelhardt, article "Die elektrolytische Perchloraterzeugung," by Billiter and Fuchs; Winteler, Z. Elektrochem. 1898, **5**, 50, 217; 1901, **7**, 635; Oechsli, *ibid.* 1903, **9**, 807; Blau and Weingand, *ibid.* 1921, **27**, 1; Couleru, Chem.-Ztg. 1906, **30**, 213; Bennett and Mack, Trans. Electrochem. Soc. 1916, **29**, 323; Howard, *ibid.* 1923, **43**, 51; Williams, Trans. Faraday Soc. 1920, **15**, 134; Knibbs and Palfreeman, *ibid.* 1921, **16**, 402, 424; Foerster, "Elektrochemie wässeriger Lösungen."

Hydrochloric Acid.—Commercial hydrochloric acid is a more or less pure solution of hydrogen chloride, HCl, in water.

Hydrogen Chloride is a colourless gas, of sp.gr. 1·2596 (air = 1) and molecular weight 36·464. Its m.p. is −111·4°C. and b.p. −85·0°C., and its critical constants are: temperature, 51·5°C.; pressure, 81·6 atmospheres; density, 0·424. Vapour pressures greater than one atmosphere are given by the formula

$$\log_{10} p = 7{\cdot}09 - \frac{1055}{T} - 0{\cdot}0105T + 0{\cdot}000014T^2$$

where T is the absolute temperature.

The heat of formation of a gram-molecule of hydrogen chloride is 22,000 cals.

Hydrogen chloride is very soluble in water, the solution being commonly known as hydrochloric acid, muriatic acid, or spirits of salt.

The following tables are abstracted from "International Critical Tables," to which reference should be made for more detailed statements of physical properties.

Weight percentage HCl.	Density (g. per millilitre) at				
	0°C.	10°C.	20°C.	50°C.	100°C.
1	1·0052	1·0048	1·0032	0·9929	0·9636
2	1·0106	1·0100	1·0082	0·9977	0·9688
4	1·0213	1·0202	1·0181	1·0073	0·9791
6	1·0319	1·0303	1·0279	1·0168	0·9892
8	1·0423	1·0403	1·0376	1·0262	0·9992
10	1·0528	1·0504	1·0474	1·0357	1·0090
12	1·0634	1·0607	1·0574	1·0453	1·0188
14	1·0741	1·0711	1·0675	1·0549	1·0286
16	1·0849	1·0815	1·0776	1·0646	1·0383
18	1·0958	1·0920	1·0878	1·0743	1·0479
20	1·1067	1·1025	1·0980	1·0840	1·0574
22	1·1177	1·1131	1·1083	1·0937	1·0668
24	1·1287	1·1238	1·1187	1·1033	1·0761
26	1·1396	1·1344	1·1290	1·1129	1·0853
28	1·1505	1·1449	1·1392	1·1224	1·0942
30	1·1613	1·1553	1·1493	1·1318	1·1030
32			1·1593		
34			1·1691		
36			1·1789		
38			1·1885		
40			1·1980		

For density determinations by hydrometers, *see* B.S.S. 718, 1936.

VAPOUR PRESSURES OF HYDROGEN CHLORIDE SOLUTIONS AT 25°C.

Weight percentage of HCl.	Partial pressure of water in mm. Hg.	Partial pressure of HCl in mm. Hg.
6	21·8	0·00131
10	20·0	0·0067
14	18·0	0·0316
18	15·4	0·148
20	14·1	0·32
22	12·6	0·68
24	11·4	1·49
26	9·95	3·20
28	8·75	7·05
30	7·52	15·1
32	6·37	32·5
34	5·35	68·5
36	4·41	142
38	3·60	277
40	2·88	515

The behaviour of aqueous solutions of HCl under varying conditions of temperature and pressure has been studied by Roscoe and Dittmar (J.C.S. 1860, **12**, 128). They found that concentrated hydrochloric acid on heating loses both gas and water, but as the proportion of HCl to H_2O is higher in the vapour than in the original liquid, the residual liquid gradually becomes weaker, until a sp.gr. of 1·101 and a percentage of 20·24 HCl are attained at a boiling temperature of 110°; the acid in this state distils without change, provided the atmospheric pressure is 760 mm. At a lower pressure the acid distilling unchanged is stronger, at a higher pressure it is weaker. A similar, but not identical, limit is attained when strong acid is exposed to the air at ordinary temperatures.

The table (p. 70*a*) from Lunge and Hurter, "Alkali-Maker's Pocket Book," 1884, gives the percentages of HCl in aqueous hydrochloric acid of various specific gravities and at a temperature of 15°.

Lunge and Hurter's "Alkali-Maker's Handbook" 1891 gives somewhat lower figures. The table in the right-hand column of p. 70 gives corrections of the hydrometer readings for varying temperatures.

The Manufacture of Hydrochloric Acid.—The Leblanc soda process, which had been gradually diminishing in importance since 1902 in Great Britain, ceased to be operated in 1920, although considerable quantities of saltcake are still manufactured for the sulphate pulp, glass making, and sodium sulphide processes (*see* "Merseyside," S.C.I., Liverpool, 1924). This decline of the Leblanc process provided a growing output for hydrochloric acid produced from electrolytic chlorine and hydrogen. There was a rapid increase in the manufacture of hydrochloric acid produced by combustion of chlorine in hydrogen which had been already commenced by Castner-Kellner Alkali Co., Ltd., in 1912. This combustion on the principle of the Bunsen burner may be carried out in open or closed burners with an excess of hydrogen.

Deg. Twaddell.	Spec. gravity.	Percentage of HCl	Grams HCl per litre.	1 cubic foot weighs lb.	1 cubic foot contains lb. of HCl.
1	1·005	1·12	11·32	62·66	0·70
2	1·010	2·12	21·45	62·97	1·34
3	1·015	3·12	31·67	63·29	1·97
4	1·020	4·11	41·99	63·60	2·61
5	1·025	5·11	52·41	63·91	3·26
6	1·030	6·11	62·93	64·22	3·92
7	1·035	7·10	73·55	64·53	4·58
8	1·040	8·10	84·27	64·84	5·25
9	1·045	9·10	95·09	65·16	5·93
10	1·050	10·09	106·01	65·47	6·61
11	1·055	11·09	117·02	65·48	7·31
12	1·060	12·09	128·14	66·09	8·00
13	1·065	13·08	139·36	66·40	8·69
14	1·070	14·08	150·68	66·71	9·40
15	1·075	15·08	162·10	67·03	10·11
16	1·080	16·07	173·62	67·34	10·83
17	1·085	17·07	185·24	67·65	11·55
18	1·090	18·07	196·96	67·96	12·28
19	1·095	19·07	208·78	68·27	13·02
20	1·100	20·06	220·70	68·59	13·76
21	1·105	21·06	232·68	68·90	14·51
22	1·110	22·06	244·80	69·21	15·27
23	1·115	23·05	257·02	69·52	16·04
24	1·120	24·05	269·34	69·83	16·79
25	1·125	25·05	281·76	70·14	17·57
26	1·130	26·04	294·28	70·46	18·35
27	1·135	27·04	306·90	70·77	19·14
28	1·140	28·04	319·62	71·08	19·93
29	1·145	29·03	332·44	71·39	20·73
30	1·150	30·03	345·36	71·70	21·54
31	1·155	31·03	358·34	72·02	22·35
32	1·160	32·02	371·44	72·33	23·16
33	1·165	33·02	384·64	72·64	23·99
34	1·170	34·02	397·94	72·95	24·82
35	1·175	35·01	411·34	73·26	25·65
36	1·180	36·01	424·84	73·57	26·49
37	1·185	37·01	438·44	73·89	27·34
38	1·190	38·01	452·14	74·20	28·20
39	1·195	39·00	466·00	74·51	29·06
40	1·200	40·00	479·84	74·82	30·00

In the open burner excess hydrogen is burnt by admission of air above the chlorine flame, resulting in an absorption system free from the danger of explosion. In the closed burner excess hydrogen carries the hydrochloric acid gas to the adsorption system. Great care is necessary in this case to avoid explosions. Solutions of hydrochloric acid made from gas thus prepared may with care be produced of analytical reagent quality.

In former days small quantities of acid were produced by decomposing common salt with sulphuric acid in cast-iron cylinders, and in order to utilise completely the relatively expensive sulphuric acid an excess of common salt was used. The solid product left in the cylinder consisted of sodium sulphate mixed with 20–30% **NaCl** and was commercially known as cylinder cake. This method of production of hydrochloric acid has, however, practically ceased.

Some time after the establishment of the Leblanc soda process in this country all the hydrochloric acid of commerce was obtained as a by-product of that process, which at first

Influence of Temperature on the Specific Gravity of Hydrochloric Acid.

0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°	95°	100°
1·168	1·165	1·163	1·160	1·157	1·154	1·152	1·149	1·147	1·144	1·142	1·140	1·138	1·136	1·133	1·131	1·129	1·127	1·125	1·123	1·121
1·158	1·155	1·153	1·150	1·147	1·145	1·142	1·139	1·137	1·134	1·132	1·130	1·128	1·126	1·123	1·121	1·119	1·116	1·114	1·112	1·110
1·148	1·145	1·143	1·140	1·137	1·134	1·132	1·129	1·127	1·125	1·123	1·120	1·118	1·116	1·113	1·111	1·108	1·106	1·104	1·102	1·099
1·138	1·135	1·133	1·130	1·127	1·125	1·122	1·119	1·117	1·114	1·112	1·109	1·107	1·104	1·102	1·100	1·097	1·095	1·093	1·090	1·088
1·128	1·125	1·123	1·120	1·117	1·115	1·112	1·110	1·108	1·106	1·103	1·101	1·099	1·096	1·094	1·091	1·089	1·086	1·084	1·081	1·079
1·118	1·115	1·113	1·110	1·107	1·105	1·103	1·101	1·099	1·097	1·094	1·093	1·090	1·088	1·085	1·083	1·080	1·078	1·075	1·073	1·070
1·108	1·105	1·103	1·100	1·097	1·095	1·092	1·090	1·088	1·086	1·084	1·082	1·080	1·078	1·076	1·073	1·071	1·069	1·066	1·064	1·061
1·098	1·095	1·093	1·090	1·087	1·085	1·082	1·080	1·077	1·075	1·073	1·071	1·069	1·067	1·065	1·063	1·061	1·059	1·057	1·055	1·053
1·088	1·085	1·083	1·080	1·077	1·075	1·073	1·070	1·068	1·066	1·064	1·062	1·060	1·058	1·056	1·054	1·053	1·051	1·049	1·047	1·045
1·078	1·075	1·073	1·070	1·067	1·066	1·063	1·061	1·059	1·057	1·055	1·053	1·051	1·049	1·048	1·046	1·044	1·043	1·041	1·039	1·037
1·068	1·065	1·063	1·060	1·057	1·055	1·053	1·050	1·048	1·046	1·044	1·042	1·040	1·038	1·036	1·034	1·033	1·031	1·029	1·027	1·025
1·058	1·055	1·053	1·050	1·047	1·045	1·043	1·040	1·038	1·035	1·033	1·031	1·029	1·027	1·025	1·023	1·021	1·019	1·017	1·015	1·013
1·048	1·045	1·043	1·040	1·037	1·035	1·032	1·030	1·027	1·025	1·022	1·020	1·018	1·016	1·014	1·011	1·009	1·007	1·005	1·003	1·001
1·038	1·035	1·033	1·030	1·027	1·024	1·022	1·019	1·017	1·014	1·012	1·010	1·008	1·005	1·003	1·001	0·999	0·997	0·995	0·993	0·991
1·028	1·025	1·023	1·020	1·017	1·014	1·012	1·009	1·007	1·004	1·002	1·000	0·998	0·995	0·993	0·991	0·989	0·987	0·985	0·983	0·981
1·018	1·015	1·013	1·010	1·007	1·004	1·002	0·999	0·997	0·994	0·992	0·990	0·988	0·985	0·983	0·981	0·979	0·977	0·975	0·973	0·971

produced hydrochloric acid gas in great excess of that which could be sold as hydrochloric acid liquor. The difficulty of the situation was aggravated by new sources of hydrochloric acid which arose when acetic acid began to be chlorinated in great quantities by the Badische Anilin und Soda Fabrik for the manufacture of monochloracetic acid and artificial indigo, and one organic compound after another came to be chlorinated. Lastly, since the output of chlorine from the electrolysis of the chlorides of potassium and sodium was not sufficiently readily taken up, processes converting electrolytic chlorine and hydrogen into hydrochloric acid are now operated on a very large scale.

Hydrochloric Acid obtained in manufacturing Sodium Sulphate (Salt Cake).—When Leblanc decomposed salt in order to obtain sodium sulphate he proposed to convert the hydrochloric acid gas evolved into ammonium chloride ; but when the Leblanc soda process was introduced into this country that part of his suggestions was not carried out, and the acid gas was regarded as possessing no value, and it was allowed to escape into the air. This continued to be the case even after that manufacture had attained a comparatively large extension, but the damage caused to the neighbourhood by the acid gases soon brought about the intervention of local authorities and courts of law, and manufacturers had to pay compensation for the damages they had done. Repeated penalties compelled the alkali manufacturers to seek means for condensing the acid gas. This was first successfully done in 1836 by Gossage's coke towers, but for many years after this there was still considerable damage done by escaping acid gas. The continued disregard by the old alkali manufacturers for the rights of their neighbours led in Belgium, in 1856, to a Parliamentary Commission, and in this country in 1863 to Lord Derby's Alkali Act, and the several subsequent Acts, by means of which British alkali makers were compelled to adopt efficient means for condensing their hydrochloric acid, and similar legislation has been to the benefit of other manufacturing countries.

The " Annual Report on Alkali, etc., Works " made by the inspectors under the Alkali Acts forms an invaluable record of all the various steps taken for improving the condensation of hydrochloric acid, and have helped to spread a better knowledge of that process and have caused manufacturers to improve it up to the highest standard of efficiency.

The Alkali Act of 1863 made it incumbent on manufacturers of salt-cake to allow no more than 5% of the hydrochloric acid to escape into the atmosphere. An additional Act of 1874 prescribed that no more than 0·2 grain of HCl might be present in a cubic foot of the gas escaping from the factory into the air. This corresponds to 0·454 g. HCl per cubic metre, or about three ten-thousandths by volume. The latter clause applies also to the chimney gases and not merely to the gases escaping directly from the condensing apparatus. Although these requirements were at first declared by many to be impossible of fulfilment, the actual results proved at once that they were quite possible, and the escapes registered by the Alkali Inspectors have averaged far below the limits assigned by the Acts. In 1885 only 2·13% of the total hydrochloric acid was allowed to escape, and the chimney and other gases escaping into the air contained only 0·10 grain HCl per cubic foot. No change has been made in the limit fixed in 1874, and the working of that Act remains satisfactory. Compare the survey of these Acts by the Chief Inspector under these Acts in J.S.C.I. 1892, **11**, 120.

Although the various processes and apparatus used for the manufacture of sulphate of soda produce gases differing within wide limits in temperature and concentration of HCl, an efficient condensation, *i.e.* practically complete absorption of the HCl in water to form a liquid acid of 1·15–1·17 sp.gr., is usually obtained.

The efficiency of the condensation of gaseous HCl in water is dependent on three considerations:

1. Temperature of the gas and of the liquid.
2. Concentration of HCl in the gases to be scrubbed and of the acid liquid to be produced.
3. Time of contact between the gas and the liquid, and the average distance between the gaseous particles and the liquid particles, and also the thickness of the liquid layer, and on its motions internal and as a whole.

On issuing from the sulphate of soda plant the acid gases require cooling. The apparatus used for this purpose depends on the temperature of the gases.

If the gases issue from the pot or pan of a handworked salt-cake furnace, the temperature is comparatively low. In this case the cooling is usually done in a row or rows of earthenware pipes. The pipes used are often unglazed, but are rendered impervious to moisture and gas by boiling in tar. In some cases the earthenware pipes are substituted by glass pipes of 12 in. diameter, made slightly taper, as shown in Fig. 27. The glass pipes are, of course, more liable to breakages by accident, and also through the effect of violent changes of temperature, than the earthenware pipes, but in sheltered positions they last well.

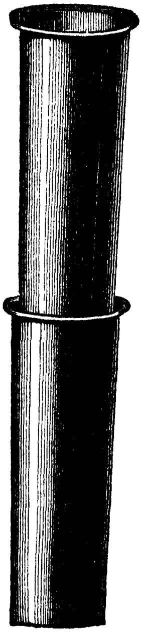


Fig. 27.

For the hotter gases issuing from an ordinary muffle-worked sulphate of soda furnace or from the cylinders of the Hargreaves process cast-iron pipes are commonly used to cool the gases to a safe temperature before passing them as before into earthenware or glass pipes. The action of the hydrochloric acid gases on cast iron is very slight at a temperature well above the condensing-point of liquid acid.

When open furnaces, whether "hand" or "mechanical" (such as the Mactear furnace), are used, the acid gases are mixed with the products of combustion, and are consequently much hotter and more dilute. Under these conditions extensive series of cast-iron pipes are used for the preliminary cooling before passing the gases into the earthenware pipes for final cooling.

The earthenware pipes used are usually 12-in. or 15-in. diameter socket pipes, the joints being made with a cement of tar and China clay. The cast-iron pipes vary from 12 to 20 in. in diameter, according to the quantity of gas and the arrangement of the cooling system of pipes; they are socket pipes, the joints being made by ramming into the socket iron filings moistened with ammonium chloride solution.

The arrangement of the cooling pipes depends on the relative positions of the salt-cake furnaces and of the acid condensers and the space available. When the salt-cake furnace is a long distance from the condensers, a single direct line of pipes may be a sufficient means of cooling; where the distance is small the necessary amount of cooling surface is obtained by adding extra lengths of pipe that run vertically up and down and that start from a small stone cistern and return to another stone cistern for the purpose of collecting any liquid deposited. The cisterns are usually made in this country of silicious sandstone found in Yorkshire, and known as "Yorkshire flag." The cisterns are composed of flags 4–6 in. thick, bound together by strong iron ties, and the joints made tight by thick indiarubber cord laid in a groove between the faces of the two stones or by a mixture of tar and fireclay, as in Figs. 28, 29, 30. By one or more of the above arrangements of pipes and cisterns the acid gases are cooled to 45°, or even to 25°. The cooling of weak gas is far more important than the cooling of strong gas.

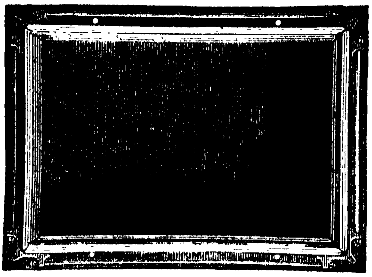


FIG. 28.

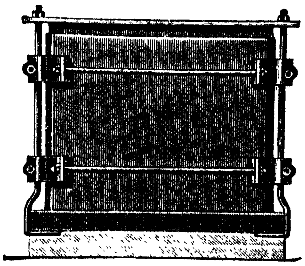


FIG. 29.

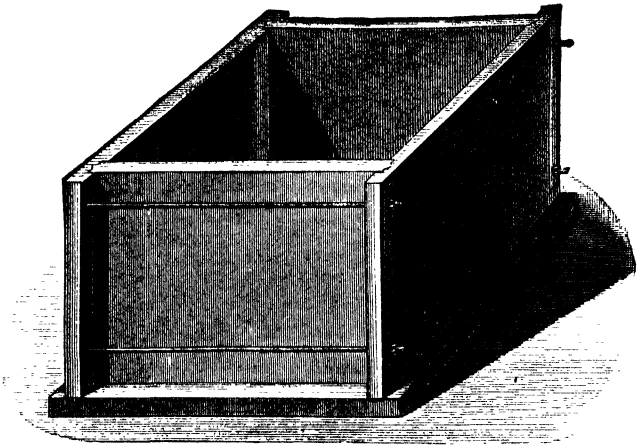


FIG. 30.

The gases next enter the apparatus where the hydrochloric acid gas is to be converted into a liquid acid of commercial strength, and that in such a manner that practically hardly a trace of acid escapes condensation.

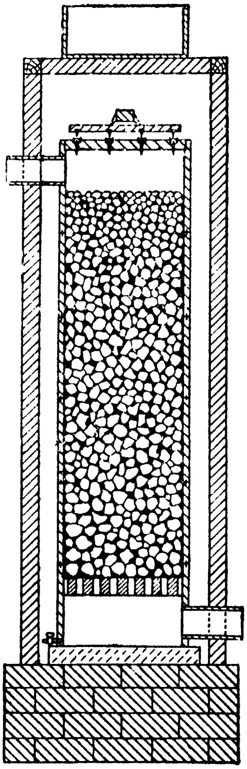


FIG. 31.

The apparatus almost universally used are tall stone towers, packed with broken coke specially arranged, down which a stream of water is allowed to trickle, and up which the gases are caused to flow (Fig. 31). These towers were invented and patented by Gossage, in 1836.

The coke tower has the merits of simplicity and, when carefully packed, of efficiency.

The comparative efficiency of various modes of treating liquids with gases has been dealt with in a series of papers by Hurter, who also gives some interesting data on coke-packed towers (J.S.C.I. 1885, **4**, 639 ; 1887, **6**, 707 ; 1893, **12**, 227, 989. *See also ibid.* 1919, **38**, 75T ; 1920, **39**, 23 ; Ind. Eng. Chem. 1924, **16**, 1215 ; Chem. Met. Eng. 1923, **29**, 146 ; Trans. Amer. Inst. Min. Met. Eng. 1919, **12**, 231 ; 1929, **22**, 165).

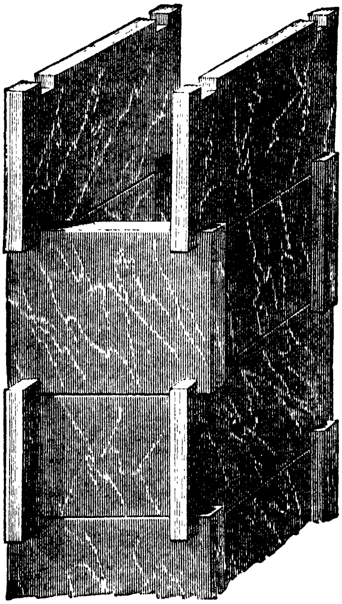


Fig. 32.

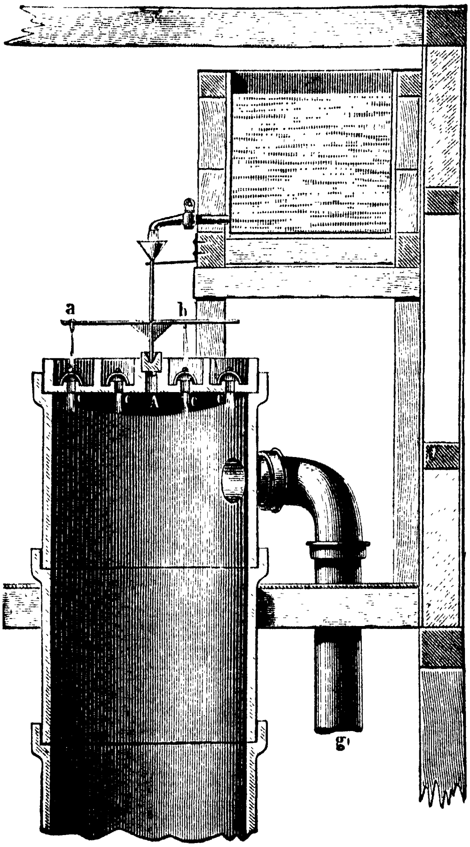


Fig. 33.

Coke towers are erections of considerable height, varying from about 40 ft. to 60 ft. The horizontal sectional area may vary from 25 to 180 sq. ft. They are provided with a grating a few feet over the bottom, on which rests the coke which forms the "packing" of the tower. This coke, which must be of as hard a quality as possible (only the best oven-coke is applicable for this purpose), is disposed in such a way that the gas is as much as possible divided in a large number of channels (none of them being so wide that the bulk of the gas can pass up through it), and that the current of gas is constantly changed in direction. For this object long pieces of coke are laid parallel in a row; the next row is made to cross the lower one, and so forth. The size of the pieces is gradually diminished from bottom to top. In order to avoid an excessive quantity of the gas passing up the side of the condenser along the wall, it is usual to place a layer of finer coke round the condenser for a few inches from the wall. By this arrangement there is effected both a great division and constant mixture of the gases, and at the same time a suitable spreading of the feeding water over a very large surface. One great advantage coke has over flints or other packings is that, owing to the roughness of its surface and its porosity, it always retains a large store of liquid, which tends to keep the working of the condensers steady under a fluctuating flow of acid gases, and to tide over difficulties occasioned by any unintentional stoppage of the liquor supply. The water (or sometimes weak acid) is fed in at the top by some contrivance assuring a uniform distribution over the whole area of the tower; and in trickling down it keeps the surfaces of the coke moist, and a very large area of contact between the gases and the liquid is thus produced. These towers are so simple to construct and so effective that of recent years there has been a growing tendency in England to do away with all cooling pipes, cisterns, wash towers, etc., and to use a couple of very large stone towers to do the whole work of cooling and condensation for two or even more salt-cake pots and furnaces. The towers are worked in series, the weak acid from the second or final tower being run down the first tower. In this way both complete absorption of the acid and the production of a strong liquid acid, *i.e.* one of over 1·15 sp.gr., are assured. To condense the acid from two hand salt-cake furnaces the two towers may each be 5 ft. square and 50 ft. high.

No difficulty is now experienced in pumping the weak acid made in the second condenser on to the top of the first condenser, either by stoneware ram pumps, ebonite ram pumps, stoneware acid eggs, or occasionally even yet by the Hazlehurst membrane pump, patented in 1876. The ascending pipe is usually of stoneware or ebonite, occasionally of lead.

Brick towers are not to be recommended, as it is practically impossible to keep the numerous joints so tight that no acid oozes out. Columns of stoneware pipes cannot be made of a large area, and, therefore, are not very well adapted to large works, at least if intended for coke towers; but they do very good service at smaller works, or as supplementary to a large condensing plant of stoneware receivers. The material mostly employed for coke towers is acid-proof sandstone or, in France, Volvic lava, just as for acid tanks. The system of joining the flags together is the same as shown in Figs. 28 and 29, or else as in Fig. 30, or as shown in Fig. 32, in which the flags are kept together by means of grooves worked in the stone, and without the aid of any ironwork, which is always a source of anxiety in acid condensers.

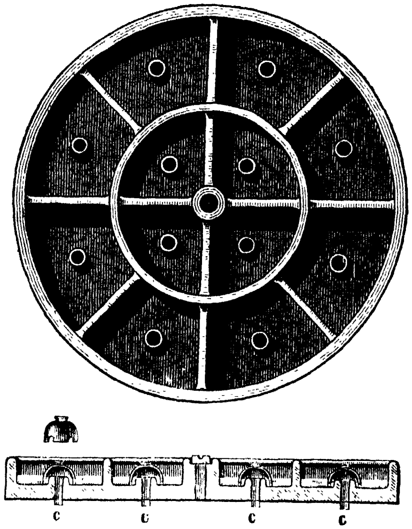


FIG. 34.

The coke towers are generally placed at a high level, and are, if necessary, put upon pillars, for the purpose of running the acid from them by gravitation either into chlorine stills or into store cisterns for sale. They must, of course, have a very secure foundation, in the construction of which not merely the great weight of the tower must be considered but also the probability that there will be now and then leakages of acid which may make the foundation unsafe. This can be avoided by asphalting the ground in such a way that any acid running down cannot penetrate into the soil, but is conveyed to a safe distance. Any damage done to the foundation, even if it amounts to much less than would cause the erection to break down altogether, is extremely injurious, because it will almost unavoidably lead to the tower getting out of level, in which case the liquid will principally descend on the lower side; thus the necessary distribution of the liquid is not attained, and the action of the condenser is most injuriously affected.

It has been already stated that the feeding of the towers with water or with weak acid must take place in such manner as to distribute it equally over the whole surface of the coke. Formerly this was generally done by a distributing wheel (shown in Figs. 33 and 34) worked by the pressure of the feed water itself. Fig. 33 shows two rotating jets (a and b), feeding the outer and inner circles of holes, causing the stream of water to reach successively every one of the holes on the top of the condenser, and thus securing a uniform distribution independently of an exact level of the top of the tower.

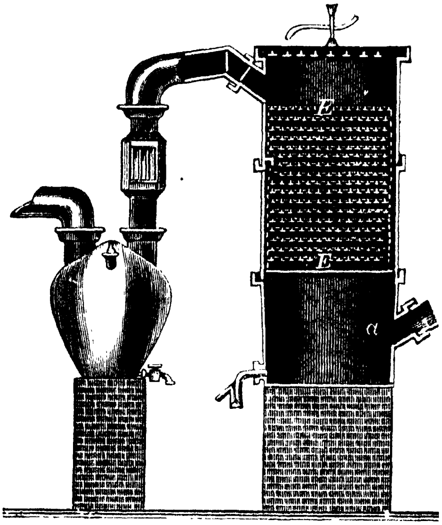


FIG. 35.

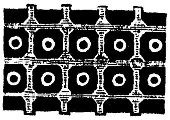


FIG. 36.

FIG. 37.

Most manufacturers have discarded these acid wheels and have introduced troughs provided with a number of overflows all at the same level, feeding the same number of water-lutes. This arrangement is indicated in Fig. 31. This figure represents a tower built as Fig. 32, the cross-hatched outer portion representing the timber framework to support the feeding cistern.

Another form of apparatus for dissolving the hydrochloric acid gas is the Lunge-Rohrmann plate tower, shown in Figs. 35, 36, and 37. It consists of an earthenware tower packed with a series of perforated plates E, E, the perforations being made to alternate in successive plates, so that each hole corresponds to a solid place in the plates just above and below. Figs. 36 and 37 show one of the plates in detail. As is to be expected, the evidence for and against the improved packings for the condensing towers is very conflicting, and as the cost of them is naturally higher, the coke-packed tower has fully maintained its position.

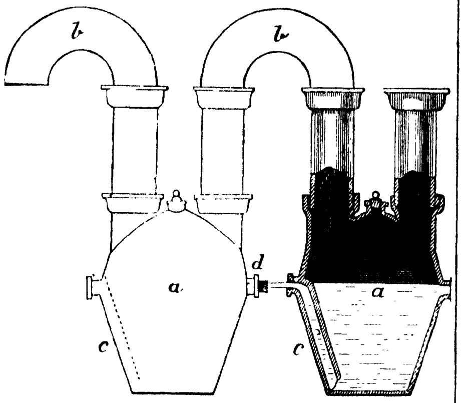


Fig. 38.

In France and Germany a somewhat different system of cooling and condensation is in general use. The earthenware and glass pipes mentioned above as being used almost exclusively in this country for the cooling of the gases are more or less completely substituted by a series of earthenware Woulfe's bottles, known technically as bombonnes or tourils (*see* Fig. 38). The scale of the drawing is too small to show that the vessel on the right is about 1 in. higher than the vessel on the left ; the liquids travel downhill from right to left, and consequently the gases are made to travel from left to right. The size of the bombonnes varies from 40 to 100 gallons. They are arranged in sets of 40 up to 100, as shown in Fig. 39, and, in spite of the relatively high temperature in the leading bombonne, eventually give a liquid acid of 1·15–1·18 sp.gr. They are made of the best stoneware, which is able to stand somewhat violent changes of temperature. After leaving the bombonnes, the acid gases are finally scrubbed with water in a coke-packed tower, similar in design but usually much smaller than those used in this country. The weak liquid acid produced in this tower supplies the stream of weak acid required by the bombonnes. The figure does not show the means of running off the strong acid from the lowest bombonnes in the series, nor the cisterns, etc., for receiving the

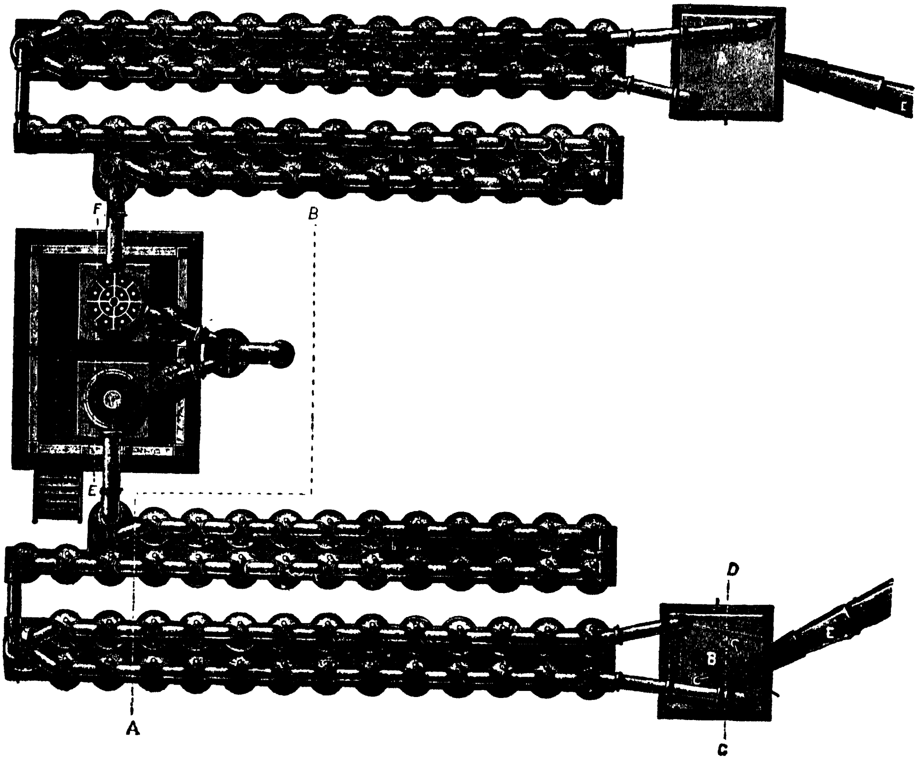


Fig. 39.

acid. Coolers and absorption plant can now be made of fused silica (Vitreosil) in the form of grids made of S-pipes, and as these can be water-cooled by sprays a reduction in the size of plant required is effected.

In the condensation of hydrochloric acid gas in water with the apparatus at present used and described above, there is little reason for difficulty in avoiding losses of HCl through incomplete absorption. The difficulty more commonly experienced is to combine the complete absorption enforced by law with a high-strength liquid acid.

The impurities found in commercial hydrochloric acid made by the above processes are, chiefly, sulphuric acid, ferric chloride, arsenic trichloride, and either free chlorine or sulphurous acid.

Sulphuric acid is the largest impurity. The hydrochloric acid condensed from the pan or pot gas is always much purer than that from the roaster gas. The quantity of *sulphuric acid* in the gases from the salt-cake furnace sometimes amounts to 2% and upwards; it was very troublesome in the Weldon, and fatal in the Deacon, chlorine process, and in some other applications of hydrochloric acid. The sulphuric acid in the salt-cake furnace gases can be removed to a large extent by a small condenser or dry scrubber before condensation. A large number of suggestions has been made for the purification of the salt-cake furnace gases, so as to render them suitable for the Deacon process, but the only one of these processes to achieve practical success is the Hasenclever process (B.P. 3393, 1883). (*See* at end of Deacon Chlorine Process.)

Arsenic gets into the hydrochloric acid through the sulphuric acid employed in its manufacture; the arsenic is thereby converted into $AsCl_3$, and passes as such into the condensing apparatus. Many plans have been proposed for its removal—most frequently a treatment with sulphuretted hydrogen or with sulphides. Bettendorff (Dingl. poly. J. 1869, 194, 253) precipitates the arsenic from concentrated hydrochloric acid by stannous chloride, and then distils the decanted acid. Duflos dilutes the acid to sp.gr. 1·13, and digests it with strips of sheet copper at 30°C. for 24 hours, and repeats this treatment with freshly scoured copper. This removes all the arsenic and the free chlorine, and reduces the ferric chloride to ferrous chloride, which remains behind on distillation. Beckurts (Fischer's Jahresb. 1884, **30,** 348) distils hydrochloric acid with ferrous chloride and removes the first 30% containing all the arsenic.

Selenium is sometimes found in such quantities in hydrochloric acid as to give trouble in its application (Davis, J.S.C.I. 1883, **2,** 157).

Hydrochloric Acid from Sources other than the Leblanc Process.—Attempts have been made to produce hydrochloric acid from many sources, notably from the residual liquors of the ammonia-soda process. A number of suggestions has been made for the direct production of HCl: (i) from $CaCl_2$; (ii) from $MgCl_2$; (iii) from NH_4Cl. In this connection compare the references given for the production of chlorine from these bodies earlier in the article. So far as is known, none of the processes is used. Mond (1883) heated the ammonium chloride with so much sulphuric acid that the acid sulphate was formed and all HCl expelled. The acid sulphate was converted by means of ammoniacal vapours into the neutral salt of commerce. O. N. Witt (1886) expelled the HCl from NH_4Cl by means of syrupy phosphoric acid, which formed ammonium phosphate. On heating this at a higher temperature the ammonia was driven out and the phosphoric acid regenerated. Jurisch (Dingl. poly. J. 1888, 267, 431) has shown that this process is not practicable, because there is no material known which resists the molten phosphoric acid, and only 63% to 86% of the NH_3 is recovered. Mond passed the vapour of ammonium chloride over nickel oxide, heated to at least 350°, which absorbed the HCl and allowed the NH_3 to pass on. After a certain time the process was changed by raising the temperature to 500° or 600° and decomposing the nickel chloride by steam, when HCl was driven off and NiO regenerated. (Several patents taken out in 1886.)

During recent years, when the chlorination of organic compounds has advanced by vast strides, the hydrochloric acid gas produced when a hydrogen atom is substituted by a chlorine atom has to be collected and utilised. The hydrochloric acid gas evolved is almost pure, easily condensed, and yields an acid quite free from the usual impurities.

Hydrochloric acid has also been produced by passing chlorine over wood at a temperature of 150°–350°, whereby charcoal is also formed (Bosnian Electricity Works at Jaice, G.P. 158086).

Lastly, hydrochloric acid has been prepared by processes inverting the practices of the last hundred years, namely, it has been prepared from its elements as a direct and definite process without the formation of by-products, or for any other reasons than its own preparation and the utilisation of the two elements formed by the electrolysis of potassium and sodium chlorides. The gases are mixed and passed over charcoal (G.P. 114219), or they are burnt together at jets (Soc. Italiana di Elettrochimica; J.S.C.I. 1915, **34,** 1142), or they are combined together by Roberts' patent (Electrochem. and Met. Ind. 1910, **8,** 704), and by this last process the acid has been manufactured in Niagara since 1914.

The conveyance and storage of hydrochloric acid of strengths varying from 27 to 40% has undergone changes in recent times following improvements in the technique of the application of rubber preparations to metal and other surfaces. Steel tanks lined with material varying from soft to hard rubber or ebonite are used for conveyance of acid in bulk (Chem. and Ind. 1924, **43,** 186R; 1932, **51,** 206, 224; Chem. Met. Eng. 1928, **35,** 673; 1929, **36,** 152; Ind. Eng. Chem. 1927, **19,** 130; Ind. Chem. 1928, **4,** 75). The familiar glass carboy is still, however, used to a large extent for the conveyance of this acid.

The applications of hydrochloric acid include the manufacture of ammonium chloride, both by neutralisation in solution and subsequent crystallisation, and by the dry process involving sublimation described in B.P. 273093, 274263, 290045 (Moore, Polack and Castner-Kellner Alkali Co., Ltd.). The older application of hydrochloric acid for the production of chlorine by the Weldon and Deacon processes is no longer of importance in Great Britain.

It is used for extracting the phosphates from bones in the production of osseine for gelatine; for preparing zinc chloride, stannous chloride, and ferrous chloride; for the preparation of pure carbonic acid from limestone; for the manufacture of aniline hydrochloride; and in the manufacture of many coal tar colours and intermediates.

In recent years the operation of cleaning (pickling) metal with hydrochloric acid prior to rolling into sheet, wire drawing, and coating with zinc, tin or lead, has been modified by the use of so-called " inhibitors " or " restrainers " sold under trade names such as *Galvene*, *Rhodine*, *Picklett*, etc. The effect of the addition of a small percentage of an " inhibitor " to hydrochloric acid is to depress the rate of solution of metal without affecting the rate of solution of the film of oxide (scale). *See* Evaluation of Pickling Inhibitors, Pirak and Wenzel, Chem.-Ztg. 1932, **56**, 193, 214.

Liquid hydrogen chloride may be stored in steel containers if the gas has been thoroughly dried. The low specific gravity of the liquid and the great weight of the cylinder militate against commercial development of this product.

F. H.

CHLORISOL. Sodium hypochlorite solution.

CHLOROCRUORIN. A pigment related to hæmoglobin which occurs in the blood plasma of certain polychæte worms (H. M. Fox, Proc. Roy. Soc. 1926, [B], **99**, 199).

CHLOROFORM, TRICHLOROMETHANE, $CHCl_3$. Chloroform was discovered by Liebig (Pogg. Ann. 1831, **23**, 242) and independently about the same time by Soubeiran (Ann. Chim. Phys. 1831, [ii], **48**, 131). Its constitution was determined by Dumas (Ann. Chim. Phys. 1834, [ii], **56**, 115), to whom the name chloroform is also due. Chloroform is very widely employed as a general anæsthetic and is an important solvent finding application in the manufacture of fats, rubber, resins, alkaloids and other products. It is a useful preservative.

Chloroform may be obtained by chlorination of a number of organic substances such as alcohol, acetone, acetaldehyde, acetophenone, turpentine, terpenes, etc., but only a few of these are of practical utility.

Chloroform was originally manufactured from ethyl alcohol, but for many years past this has been replaced by acetone. Owing to the much cheapened production of acetaldehyde at the present time chlorination of the latter product bids fair to displace the use of acetone. According to Feyer (Z. Elektrochem. 1919, **25**, 115) the formation of chloroform from alcohol by the action of bleaching powder is represented by the following equations, the reaction taking place in three stages involving oxidation and formation of aldehyde, as follows:

$$(1)\ CH_3{\cdot}CH_2OH+HOCl = CH_3{\cdot}CHO+H_2O+HCl$$

$$(2)\ CH_3{\cdot}CHO+3HOCl = CHCl_3+H{\cdot}COOH+2H_2O$$

$$(3)\ H{\cdot}COOH+HOCl=CO_2+H_2O+HCl$$

The action of bleaching powder on acetone appears to be best represented by the equation:

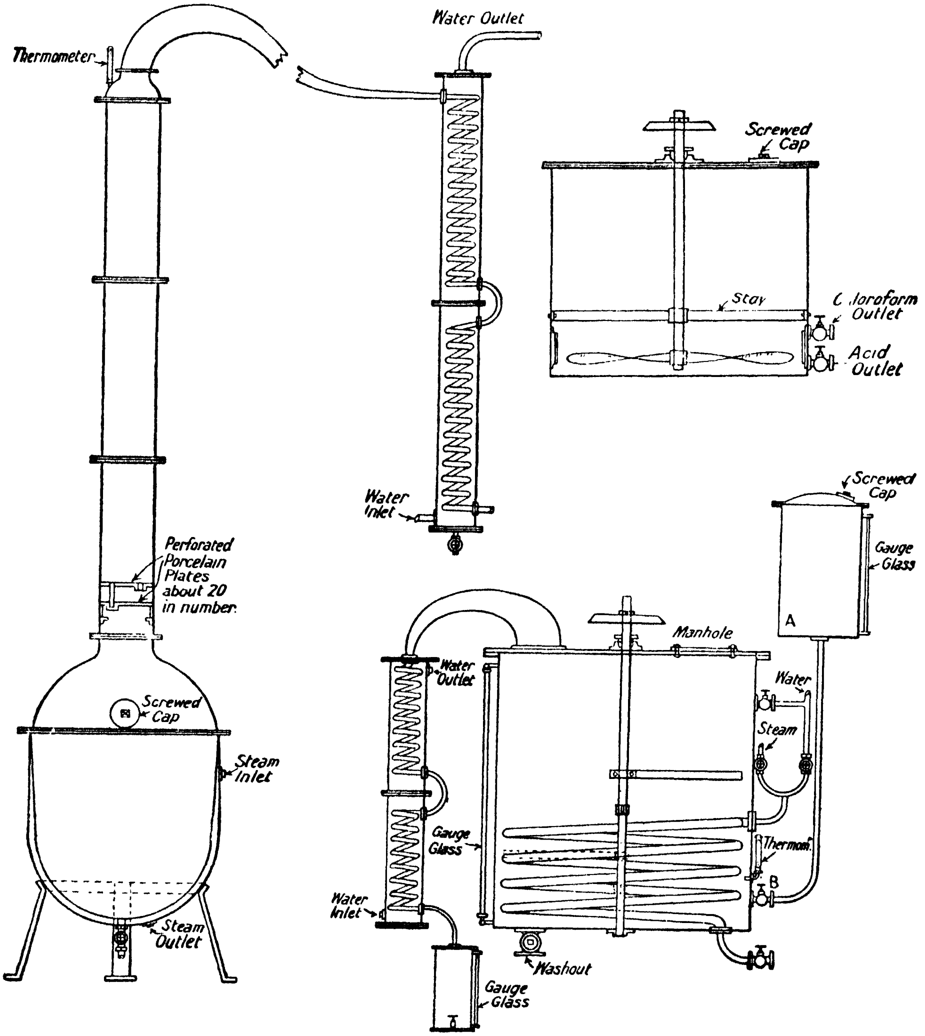
$$2CO(CH_3)_2+6CaOCl_2 = 2CHCl_3+(CH_3{\cdot}COO)_2Ca+2Ca(OH)_2+3CaCl_2$$

Manufacture of Chloroform from Acetone and Bleaching-powder.—This is the process most generally employed. The method differs in minor details with the various manufacturers, but the following may be taken as representative. The reaction is carried out in a cast-iron still of about 800 gallons capacity, which is provided with stirring gear, steam-coils, and cooling coils, and is connected with a condenser; 300 gallons of water are run into the still, and 800 lb. of bleaching powder are added through a manhole, which is then securely bolted down. During addition of the bleaching powder the mixture is very thoroughly stirred. (In some processes the mixing is carried out in a separate vessel, and the suspension is strained from the larger unbroken lumps of bleaching powder before being allowed to run into the still.) The container (*A* in the diagram shown on p. 78) is charged with 70 lb. of acetone, which is then slowly run into the bottom of the still by means of the valve *B*. The introduction of the acetone is accompanied by a rise of temperature which is not allowed to exceed 110°F., cooling being effected if necessary by stopping the flow of acetone and circulating cold water through the cooling coil in the still. When all the acetone has been introduced the contents of the still are raised to 134°F. At this temperature chloroform begins to distil over. The temperature is then very gradually raised to 150°F., so as to keep the chloroform steadily distilling. Towards the end of the reaction the mixture is stirred and the temperature raised until no more chloroform distils over.

The crude chloroform obtained is separated and purified first by agitation with concentrated sulphuric acid. This operation is carried out in the vessel shown in the diagram ; 1,500 lb. of crude chloroform are introduced into the vessel and thoroughly stirred, by means of the agitating gear shown, with 600 lb. of sulphuric acid. The stirring is continued until a sample of the chloroform when thoroughly shaken with pure concentrated sulphuric acid does not impart the slightest colour to the latter. The time required for complete purification is usually about 3 hours. The chloroform is next separated from the sulphuric acid and finally distilled over lime. The yield obtained from the above quantities averaged from over 2,000 batches was 124 lb., the highest yield in any one case being 131 lb. Variation in yield is attributed to the varying composition of the bleaching powder, though doubtless other factors influence the result.

Bleaching powder containing less than 33% of available chlorine gives unsatisfactory results, while samples containing more than 35% of chlorine are also often unsatisfactory. The best results appear to be obtained with bleaching powder containing about 34% of available chlorine.

Manufacture from Acetaldehyde.—This consists essentially of the treatment of an aqueous solution of acetaldehyde with a solution of hypochlorite. A yield of 80% of chloroform is claimed for the following process (G.P. 347460). A 20% aqueous solution of acetaldehyde is allowed to flow into a solution of bleaching powder containing 93 g. of active chlorine per litre. The mixture is vigorously stirred and the temperature maintained at 45°C. After addition is complete stirring is continued for a short time, the solution neutralised, and the chloroform separated by distillation. Purification is effected in the usual way (*see also* G.P. 339914 and F.P. 521700). A continuous process for the production of chloroform, in which a mixture of acetone and acetaldehyde is treated with a solution of hypochlorite containing 40 g. of active chlorine or more per litre, is described in U.S.P. 1915354. The mixture of the solutions is led into a reaction vessel provided with a stirrer and maintained at a temperature of 70°-80°C. The chloroform is removed by leading steam into the mixture as it passes into a separating vessel, the chloroform distilling off through a condenser while the residual liquors are continuously discharged.



Other Methods of Manufacture.—Chloroform has been manufactured in America from carbon tetrachloride by reduction with nascent hydrogen. The most usual method is to stir vigorously a mixture of the tetrachloride and finely divided iron in water, the reaction being initiated by the addition of a small amount of hydrochloric acid (U.S.P. 753325, 1107025). Numerous attempts have also been made to manufacture chloroform by chlorination of methane (natural gas), but so far without any pronounced success. A number of patents have also dealt with electrolytic methods of production from alcohol or acetone, but very little appears to have been made in this way.

Chloroform is a heavy colourless liquid with a characteristic odour. It has b.p. 61·2° (Baskerville and Hamor, Ind. Eng. Chem. 1912, **4**, 278; Wade and Finnemore, J.C.S. 1904, **85**, 946), f.p. $-64{\cdot}19°$ (Keyes *et al.* J.C.S. 1923, **124**, II, 376), d_4^{15} 1·4989 (Baskerville and Hamor, *l.c.*).

It is not inflammable but burns with a greenish smoky flame when mixed with alcohol and the mixture ignited. It is slightly soluble in water (0·5%) and miscible with most organic solvents.

When a primary amine is heated with chloroform in an alcoholic solution of potassium hydroxide an *iso*cyanide is formed:

$$CHCl_3+RNH_2+3KOH = RNC+3KCl+3H_2O$$

The reaction employing aniline as the primary amine affords a ready method of detecting chloroform in considerable dilution (1–5,000 to 6,000) the characteristic odour of phenyl isocyanide being easily recognised. The reaction is, however, not specific, being given by bromoform, iodoform, chloral, etc. Chloroform also reduces Fehling's solution.

Anæsthetic Chloroform.—Chloroform for anæsthetic purposes is required to be of a very high standard of purity and the various pharmacopœias detail the tests for a number of impurities which may occur in the product and render it unsuitable for use as an anæsthetic. Pure chloroform under the influence of light, air, and moisture is decomposed more or less rapidly according to conditions, the main products of decomposition being carbonyl chloride (phosgene) and hydrochloric acid, according to the equations:

$$CHCl_3+H_2O+O_2=COCl_2+HCl+H_2O_2$$

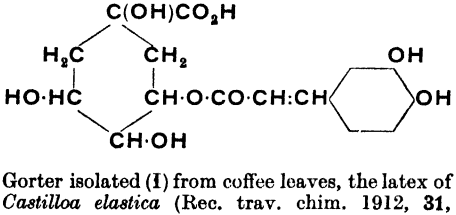
$$CHCl_3+H_2O_2=COCl_2+HCl+H_2O$$

The presence of a small amount of ethyl alcohol in the chloroform has been shown to exert a very definite stabilising effect, and most pharmacopœias specify the addition of alcohol for this purpose. The amount permitted by the "British Pharmacopœia" is from 1–2%. According to Baskerville and Hamor (Ind. Eng. Chem. 1912, **4**, 368, etc.) alcohol appears to act by reason of its property as a reducing agent, oxidation of alcohol taking place in preference to that of chloroform. At the same time the products of oxidation appear to exert a retarding action and chloroform containing the amount of alcohol mentioned above, when properly packed and stored so that the action of light and air is reduced to a minimum, will keep in a satisfactory condition for years. The theory of the action of alcohol is supported by the fact that many other organic reducing substances also inhibit the decomposition of chloroform. The action of such substances for the preservation of chloroform for anæsthetic purposes has been investigated by Bodendorf (Apoth.-Ztg. 1929, **44**, 351) by exposing chloroform containing the suggested preservative to the action of light from a quartz lamp, when it was conclusively shown that alcohol is the most satisfactory stabilising agent.

For the estimation of chloroform in small amounts W. H. Cole (J. Biol. Chem. 1926, **71**, 173) has suggested a colorimetric method based on the colour reaction obtained with pyridine and caustic soda. The method is said to be capable of detecting 0·001% of chloroform in solution, but its use for the determination of the compound in biological fluids has been criticised by Yeager (Proc. Soc. Exp. Biol. Med. 1929, **26**, 403). It has, however, been modified for the purpose by Gettler and Blume (Arch. Path. 1931, **11**, 554). A colorimetric method for the estimation of chloroform in alcoholic solutions, tinctures, etc., has been described by Moffitt (Analyst, 1933, **58**, 2). It depends upon the production of a blue colour at the ordinary temperature with β-naphthol and potassium hydroxide, a reaction which readily lends itself to colorimetric comparison. A similar colour is given with α-naphthol, but in this case the reaction is also given by other chlorinated compounds. With β-naphthol, however, closely related compounds such as carbon tetrachloride, dichloroethylene, ethylene chloride, etc., give no colour.

A. J. E.

CHLOROGENIC ACID (I), Caffetannic Acid (II). The substance described as (I) by Payen (Ann. Chim. 1849, [iii], **26**, 108) is now recognised to be the chief constituent of Rochleder's (II) (Annalen, 1846, **59**, 300, and many later authors). The alcoholic extract of Liberian coffee yielded on evaporation 3·3% of crystalline potassium-caffeine chlorogenate, which loses caffeine when shaken with moist chloroform; dilute sulphuric acid then liberates (I), $C_{16}H_{18}O_9$, needles, with $\frac{1}{2}H_2O$, m.p. 208°, $[\alpha]_D$ $-35{\cdot}2°$ (Gorter, Annalen, 1908, **358**, 327; 1911, **379**, 111; Freudenberg, Ber. 1920, **53**, [B], 232). Tannase from *Aspergillus niger* splits the acid into quinic acid and caffeic acid, indicating a depside formula (Freudenberg, *l.c.*). The position of the linkage was determined by H. O. L. Fischer and Gerda Dangschat (Ber. 1932, **65**, [B], 1037), who assigned to (I) the constitution 3-[3:4-dihydroxycinnamoyl]-1-quinic acid,



Gorter isolated (I) from coffee leaves, the latex of *Castilloa elastica* (Rec. trav. chim. 1912, **31**, 281), sunflower seeds (Arch. Pharm. 1909, **247**, 436), and from *Strychnos nux vomica* (*ibid. idem.* 197). If Gorter's colour reaction (*ibid.* **247**, 187; Annalen, 1911, **379**, 111) could be trusted, (I) is widely distributed in the vegetable kingdom (*cf.* Charaux, J. Pharm. Chim. 1910. [vii], **2**, 292 ; van der Haar, Pharm. Weekblad, 1920, **57**, 194). Caffeic acid gives the same coloration (Freudenberg, *l.c.*). The estimation of (I) in coffee has been studied (B, 1934, 40, 119, 379, 426, 524, 700, 779, 985). In spite of the name (II), (I) does not precipitate a dilute gelatin solution, but when warmed with a 10% solution gives a precipitate on cooling (Freudenberg, *l.c.*).

J. N. G.

CHLOROPHYLL. The colouring matter of green leaves. A mixture of two closely allied substances—chlorophyll-*a*, $C_{55}H_{72}O_5N_4Mg$, and chlorophyll-*b*, $C_{55}H_{70}O_6N_4Mg$.

It occurs widely distributed in plants, mainly in the leaves and green stems, in the *chloroplasts*, together with the yellow (carotenoid) pigments carotene and xanthophyll. It is present in both green and brown algæ, the latter of which also contain another carotenoid, fucoxanthin. It is the active catalyst in the photosynthesis of sugars from carbon dioxide and water, and is therefore of fundamental importance. It is the only enzyme of known chemical structure.

For the bulk of our knowledge of chlorophyll, we are indebted to the brilliant investigations of Richard Willstätter and Hans Fischer, and their collaborators.

Historical.—(*See* Willstätter and Stoll, " Untersuchungen über Chlorophyll," Berlin, 1913 [1] ; Marchlewski, " Chemie der Chlorophylle," Braunschweig, 1909). Of early attempts to isolate the green leaf pigment, those of Berzelius (Annalen, 1838, **27**, 296) and Verdeil (Compt. rend. 1851, **33**, 699) may be mentioned. The latter believed that it contained iron, like the hæmoglobin of blood, an idea which persisted for some time. Other erroneous conceptions which complicated early work were that the pigment contained phosphorus and potassium. Valuable exploratory work was subsequently carried out by Schunck (Proc. Roy. Soc. 1885, **38**, 336, etc.), and Schunck and Marchlewski (Annalen, 1894, **278**, 329). It was thought at one time that samples of chlorophyll isolated from different sources and at different seasons were not identical. This was disproved by Willstätter, whose investigations (1906–1913) led to a general clarification of the subject. More recently, the chemistry of chlorophyll has been examined with great thoroughness by Hans Fischer (1929–1936) with the result that the structure is now certain in main outline and only a few details remain to be settled. Chlorophyll has not yet been synthesised, although progress in this direction has been made. The exact rôle of the pigment in the photosynthetic process remains to be settled.

Extraction.—Both fresh and dried green leaves can be used as sources of chlorophyll. The common nettle, first used by Stokes (1852), is a convenient source, being cheap, rich in chlorophyll, readily dried while maintaining its colour well, and being poor in enzymes. Extraction is best carried out at room temperature with acetone containing 15–20% of water (Willstätter). The acetone solution is treated with light petroleum and extracted with water to remove the bulk of the acetone and then with methyl alcohol to remove xanthophyll. Finally the petroleum solution is washed free from acetone and methyl alcohol with water ; this precipitates the chlorophyll, which is filtered off by means of a column of talc. The talc is washed with petroleum (to remove all carotene) and the chlorophyll extracted with ether. The ethereal solution is dried by means of sodium sulphate and the chlorophyll precipitated by the addition of petroleum. (For details *see* Willstätter, " Chlorophyll," Chapters 3 and 4.) The extraction with alcohol, which is used for certain technical purposes, leads to a chemical change (*see below*).

A commercial chlorophyll is manufactured for the colouring of soap, oils and perfumes. For this purpose green leaves (nettles) are extracted with ethyl alcohol, the solvent distilled and the residue extracted with benzene. The residue from this second extraction is the basis of the commercial product. A water-soluble pigment is obtained by hydrolysis with caustic soda. This material has a yellowish-green shade ; to obtain a bluish-green, 1% of copper sulphate is added in the original alcoholic extraction. The product presumably contains copper in place of the magnesium atom present in the chlorophyll molecule (*see below*).

The chlorophyll content of dried nettle leaves is about 0·8% and about 80% of this (6·5 g. from 1 kg. of leaves) can be extracted by Willstätter's procedure.

The chlorophyll so obtained is a mixture of the -*a* and -*b* components, which are present in land plants in the proportion of about 3 : 1. In brown algæ the proportion of the -*b* form is much smaller. In spite of claims to the contrary, it is probable that only two forms of chlorophyll exist (Winterstein and Schön, Z. physiol. Chem. 1934, **230**, 139 ; but *see* Conant and Dietz, Nature, 1933, **131**, 131; J. Amer. Chem. Soc. 1933, **55**, 839). Chlorophyll-*b* can be removed from a petroleum solution of the mixed pigment by extraction with 90% methyl alcohol (Willstätter and Isler, Annalen, 1912, **390**, 269), a method which has been improved by Stoll and Wiedemann (Helv. Chim. Acta, 1933, **16**, 739). Another method of separation is by chromatographic adsorption on a column of calcium carbonate or preferably, powdered sugar (Tswett, Ber. 1908, **41**, 1352 ; Winterstein and Stein, Z. physiol. Chem. 1933, **220**, 263). By this method the two forms of chlorophyll can be separated from one another and from the carotenoids which accompany them in the plant. In the examination of structure it is usual to separate not the two forms of chlorophyll itself, but the corresponding degradation products, the phæophorbides, which are easily separated by acid fractionation (*see below*).

Physical Properties.—The mixed chlorophyll obtained by acetone extraction is a dark green waxy solid. Pure chlorophyll-*a* is obtained microcrystalline by adding petroleum to its ethereal solution. Slow evaporation of a solution in a mixture of these solvents gives thin lanceolate leaflets. Chlorophyll-*b* can be obtained similarly in a microcrystalline form. In powder form chlorophyll-*a* appears bluish-black, it gives a green streak and has a steel-blue reflex. The powder of the *-b* form is very dark green. Chlorophyll-*a* is soluble in ether, absolute ethyl alcohol, acetone, chloroform, carbon disulphide and benzene ; moderately soluble in cold methyl alcohol, more soluble in hot ; very sparingly soluble in light petroleum, but the solubility is raised considerably by the addition of a little alcohol. It is practically insoluble in alcohols containing 20% of water. The solutions are bluish-green with a red fluorescence. The solubility of chlorophyll-*b* resembles that of the *-a* component, but is slightly lower throughout. The difference is most marked in the case of light petroleum. The solutions are yellow-green to green with a brownish-red fluorescence.

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[1] Referred to henceforward as Willstätter, " Chlorophyll."

Chlorophyll-*a* sinters and melts between 117° and 120° ; chlorophyll-*b* sinters between 86° and 92° and melts to a thick liquid between 120° and 130°.

Absorption Spectra.—Both components of chlorophyll have complex absorption spectra. The main areas of transmission are in the region of 500$m\mu$ (green) and 700$m\mu$ (red). The main bands in the spectrum of chlorophyll-*a* have maxima at 662$m\mu$ and 433$m\mu$; there are also strong bands at 612$m\mu$ and 458$m\mu$ and weaker bands between the green and orange-red. The end-absorption commences at about 415$m\mu$. The absorption spectrum of chlorophyll-*b* differs from this principally in having the main red band split into two and in the deepening of the band in the blue at 457$m\mu$, which becomes the strongest band. For further details, *see* Willstätter, "Chlorophyll," p. 169 ; Hans Fischer, Oppenheimer's "Handbuch der Biochemie," 1923, p. 351 ; Conant and Kamerling, J. Amer. Chem. Soc. 1931, **53**, 3522 ; and a series of papers by Stern, Wenderlein and their collaborators, Z. physikal. Chem. (A), 1934, **170**, 337 ; 1935, **174**, 81, 321 ; 1936, **175**, 405 ; **176**, 81 ; **177**, 40, 165, 365, 387.

Optical Activity.—It was thought for a long time that chlorophyll was optically inactive, but in 1933 Stoll and Wiedemann (Helv. Chim. Acta, 1933, **16**, 307) using red light (λ, 720$m\mu$) found that both chlorophyll-*a* and *-b* were lævorotatory with $[\alpha]_{720}^{25}$ about $-265°$. The phytyl- and magnesium-free derivatives, the phorbides (*see below*), were also active. Fischer and Stern have confirmed and extended these observations (Annalen, 1935, **519**, 58 ; **520**, 88). There is a difference between these workers' observations on the ease of racemisation of the solutions. The porphyrins derived from chlorophyll (*see below*) are all optically inactive.

Reactions and Structure.—As stated above, the two components of chlorophyll have the formulæ:

$$\text{chlorophyll-}a,\ C_{55}H_{72}O_5N_4Mg$$
$$\text{chlorophyll-}b,\ C_{55}H_{70}O_6N_4Mg$$

Chlorophyll-*b* contains one more atom of oxygen and two less of hydrogen than chlorophyll-*a* ; actually it contains an aldehyde group in place of a methyl group.

"*Crystalline chlorophyll,*" *chlorophyllides.*—It was found by Willstätter and Utzinger (Annalen, 1911, **382**, 129) that when ethyl alcohol was used in place of acetone to extract green leaves, the pigment was isolated as bluish-green crystals. This involves a chemical change catalysed by an enzyme, *chlorophyllase*, present in the leaf. The change is shown below for the *-a* component

$$\underset{\text{Chlorophyll-}a}{C_{34}H_{33}O_3N_4Mg{\cdot}CO_2C_{20}H_{39}}+C_2H_5OH$$
$$\rightarrow \underset{\text{I.}}{C_{34}H_{33}O_3N_4Mg{\cdot}CO_2C_2H_5}+C_{20}H_{39}OH$$

The compound (I), ethyl chlorophyllide, is the main constituent of crystalline chlorophyll. The other reaction product is *phytyl alcohol*, a wax-like, unsaturated primary alcohol. The structure of this has been proved to be

$$Me_2CH{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe[CH_2]_3{\cdot}CMe{:}CH{\cdot}CH_{26}OH$$

both by degradation and synthesis (F. G. Fischer and Löwenberg, Annalen, 1929, **475**, 183).

A similar enzymatic alcoholysis with methyl alcohol yields *methyl chlorophyllide*,

$$C_{34}H_{33}O_3N_4Mg{\cdot}CO_2{\cdot}CH_3.$$

It was found by Willstätter, Hocheder and Hug (Annalen, 1909, **371**, 1) that the same phytyl alcohol was obtained by the decomposition of the chlorophyll from a large number of different plants. It is the presence of the phytyl group in the molecule which enables chlorophyll to form colloidal solutions.

Phæophorbides (Willstätter and Hocheder, Annalen, 1907, **354**, 205).—Hydrated oxalic acid in alcohol leads to a straightforward elimination of magnesium from chlorophyll. The product is an olive-brown solid, phæophytin (II). Similarly, treatment of methyl chlorophyllide with a 17% solution of hydrochloric acid in ether leads to the formation of methyl phæophorbide (III). If stronger acids are used, the phytyl or methyl esters are also hydrolysed with the formation of the corresponding free acid, phæophorbide (IV) :

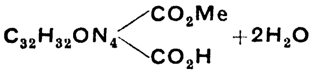
$$\begin{tikzcd}
C_{34}H_{33}O_3N_4Mg{\cdot}CO_2{\cdot}C_{20}H_{39} \arrow[r, "\text{Oxalic acid}"] \arrow[d, "\text{MeOH, enzyme}"] & C_{34}H_{33}O_3N_4H_2{\cdot}CO_2{\cdot}C_{20}H_{39}\ \text{II.} \arrow[d, "HCl"] \\
C_{34}H_{33}O_3N_4Mg{\cdot}CO_2Me \arrow[d, "\text{dil. }HCl"] & \underset{\text{IV.}}{C_{34}H_{33}O_3N_4H_2{\cdot}CO_2H} \\
\underset{\text{III.}}{C_{34}H_{33}O_3N_4H_2{\cdot}CO_2Me} \arrow[ur, dashed, "\text{stronger }HCl"'] &
\end{tikzcd}$$

The above reactions are shown for the -*a* series. In actual practice a mixture of phæophorbides-*a* and -*b* are obtained. These can be separated by partition between ether and hydrochloric acid as follows :

Acid Separation (Willstätter, " Chlorophyll," p. 262).—This is a useful general method for the separation of substances of similar structure by taking advantage of small differences in basicity. The mixture is dissolved in ether and extracted with hydrochloric acid in gradually increasing strength. The *acid number* of the substance is the percentage concentration of hydrochloric acid which extracts two-thirds of the substance from an equal volume of its ethereal solution. For example, methyl phæophorbides-*a* and -*b* have acid numbers of 16 and 21 respectively. The former is completely extracted by 18% acid, the latter requires 23% acid. Extraction of an ethereal solution of a mixture with 17% acid leads to an almost complete separation. The procedure cannot be used with compounds containing magnesium, such as chlorophyll itself, or the chlorophyllides, unless the elimination of metal is immaterial.

From this point the structure and reactions of the more fully studied -*a* component of chlorophyll and its degradation products will be dealt with exclusively.

Chlorin-e.—Two of the five oxygen atoms of chlorophyll-*a* are in a carboxyl group which carries the phytyl group. Two other oxygen atoms are present in the form of a carbomethoxyl group. This is comparatively hard to hydrolyse by acids, but if phæophorbide-*a* is boiled very rapidly with methyl alcoholic potash for 30 seconds a tribasic acid *chlorin*-e is obtained. This yields a characteristic trimethyl ester (Willstätter and Utzinger, Annalen, 1911, **382**, 171). The change involves a hydrolysis of the stable carbomethoxyl group and a conversion of the fifth oxygen into a carboxyl group :



$$C_{32}H_{32}ON_4\begin{cases}CO_2Me\\CO_2H\end{cases} + 2H_2O$$

Phæophorbide-*a*

$$\rightarrow C_{31}H_{33}N_4(CO_2H)_3 + MeOH$$

Chlorin-*e*.

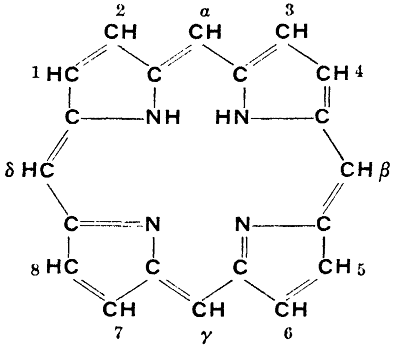
The implication is that the fifth oxygen atom is part of a pseudo-acidic group. From H. Fischer's work this is a cyclic β-ketonic ester grouping. It was previously thought to be a lactone group. Essentially the same change has been brought about by the conversion of methyl phæophorbide-*a* to the trimethyl ester of chlorin-*e* by the action of diazomethane in methyl alcohol (H. Fischer and co-workers, Annalen, 1932, **498**, 194 ; 1933, **506**, 107).

Hydrolysis of chlorophyll-*a* itself with potash under non-oxidising conditions gives a similar reaction, but in this case the product is the potassium salt of iso*chlorophyllin*-a,

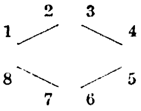
$$C_{31}H_{31}N_4Mg(CO_2K)_3.$$

This is converted into chlorin-*e* by treatment with acids, the atom of magnesium being exchanged for two of hydrogen.

Drastic Degradation by Alkali.—Alkalis at high temperatures convert the magnesium-free derivatives of chlorophyll, particularly chlorin-*e*, into a series of *porphyrins*. These are red, crystalline solids with low acid numbers, and are based on the common structural unit, *porphin* (V) :



V.



V*a*.

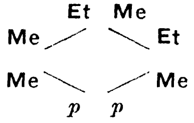
The conventional lettering and numbering of the porphin group is shown above, and a convenient abbreviation in V*a*. Porphin and the porphyrins (which are its derivatives, substituted in the numbered positions) possess a characteristic type of absorption spectrum, and the power to form stable derivatives with metals, in which the two imino-hydrogen atoms are substituted, *e.g.* by a divalent metal atom. The porphin nucleus exhibits a resemblance to the aromatic type (*see* Linstead, Chem. Soc. Annual Rep. 1935, **32**, 359).

The porphyrins isolated from chlorophyll derivatives are tabulated below. They all contain the following substituents : hydrogen atoms on the *a*-, β-, and δ- carbon atoms, methyl groups on the 1-, 3-, 5-, and 8- carbon atoms, ethyl groups on the 2- and 4- carbon atoms. The other substituent groups are indicated in the table :

PORPHYRINS FROM CHLOROPHYLL DERIVATIVES

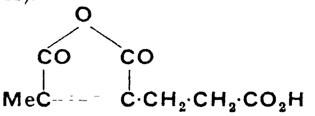
Name and formula.	Substituents (p = —$CH_2{\cdot}CH_2{\cdot}CO_2H$). 6-	7-	γ-
Rhodoporphyrin, $C_{30}H_{32}N_4(CO_2H)_2$	CO_2H	*p*	H
Phylloporphyrin, $C_{31}H_{35}N_4(CO_2H)$	H	*p*	Me
Pyrroporphyrin, $C_{30}H_{33}N_4(CO_2H)$	H	*p*	H
Phylloætioporphyrin, $C_{31}H_{36}N_4$ . . .	H	Et	Me
Pyrroætioporphyrin, $C_{30}H_{34}N_4$ . . .	H	Et	H

Pyrroætioporphyrin, the last-named and simplest of these compounds, was at one time believed to be identical with the oxygen-free ætioporphyrin isolated by degradation of the hæmin of blood (ætioporphyrin-III). Although this is not the case, the substances are very closely related, the ætioporphyrin from the blood pigment having an ethyl group in place of a hydrogen atom on C_6. All these structures have been confirmed by synthesis (H. Fischer and coworkers, Annalen, 1928, **461**, 221 ; 1929, **473**, 211 ; **475**, 241 ; 1930, **480**, 109, 189 ; **482**, 232). Pyrroporphyrin from chlorophyll has been converted into mesoporphyrin (VI), a degradation product of hæmin.

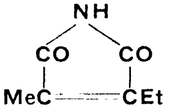


VI.

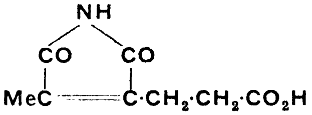
Drastic Degradation to Pyrroles.—Derivatives of chlorophyll can be converted into simple pyrrole derivatives by two methods, involving oxidation and reduction respectively. Marchlewski (J. pr. Chem. 1902, [ii], **65**, 161) oxidised phylloporphyrin with chromic acid to the anhydride (VII). Willstätter and Asahina (Annalen, 1910, **373**, 227) oxidised rhodo-, phyllo-, and pyrro-porphyrins and chlorin-*e* to a mixture of methylethyl maleinimide (VIII) and hæmatic acid (IX, *i.e.* the imide corresponding to VII).



VII.



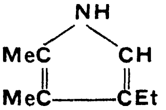
VIII.



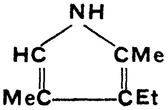
IX.

For recent work on this subject, *see* Fischer and Breitner (Annalen, 1936, **522**, 151).

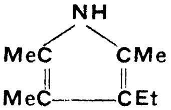
Willstätter and Asahina (Annalen, 1911, **385**, 188) reduced phylloporphyrin with hydrogen iodide and acetic acid to a mixture of alkyl pyrroles containing hæmopyrrole (X), kryptopyrrole (XI), and phyllopyrrole (XII) :



X.

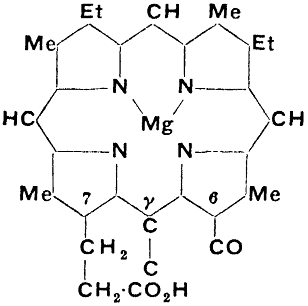


XI.



XII.

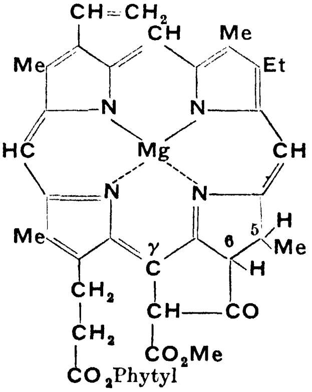
The facts enumerated above lead to the following skeleton structure (XIII) for chlorophyll-*a* :



XIII. (Double bonds and pyrrole carbon atoms omitted for clarity.)

The magnesium atom is attached to nitrogen atoms because it is known that oxygen-free compounds, such as the ætioporphyrins, can form magnesium derivatives. The carbon atom on C_γ is the source of the γ-methyl group of phylloporphyrin, and the CO group on C_6 is the source of the 6-carboxyl group in rhodoporphyrin.

The full formula for chlorophyll-*a*, proposed by H. Fischer (Annalen, 1935, **520**, 88), is as follows :



XIV. (Phæophorbide-*a* has the same formula with H, H for Mg, and H for phytyl.)

It is not possible in the present article to give the complete evidence justifying the various structural features of this formula, other than those already discussed. Some of the more important points are discussed below, and references are given to the original memoirs. The reader is also referred to the general bibliography at the end of the article.

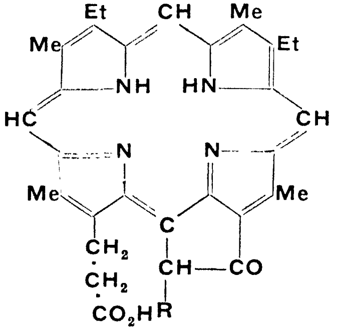
(1) The general arrangement is the same as that of the skeleton structure (XIII). Fischer's

formula (XIV) is not, however, based on a simple porphin structure, because the original double bond between C_5 and C_6 is saturated.[1] Chlorophyll is therefore a dihydroporphin derivative, as first suggested by Conant (Conant and Kamerling, *l.c.*, Conant, Chow and Dietz, J. Amer. Chem. Soc., 1934, **56**, 2185). These saturated asymmetric carbon atoms are the seat of the optical activity. In a recent paper (Annalen, 1936, **525**, 259) Fischer and Lautsch have succeeded in removing the two " extra " hydrogen atoms quantitatively by means of silver oxide or silver acetate in acetic acid.

(2) Carbon atoms 6- and γ- are connected to form a *cyclo*-pentane ring. This ring contains a pseudo-acidic β-ketonic ester grouping, in which is the carbomethoxyl group which, as has already been mentioned, resists hydrolysis. It is this ring which is opened when chlorin-*e* is formed from phæophorbide-*a*. The presence of the keto-group was proved independently by Fischer *et al.* (Annalen, 1934, **508**, 224) and Stoll and Wiedemann (Helv. Chim. Acta, 1934, **17**, 163) by the preparation of an oxime from methyl phæophorbide-*a*. The presence of the *cyclo*pentane ring is deduced from Fischer's work on *phæoporphyrin-a_5*,[2]

$C_{34}H_{34}O_5N_4$, (XV, $R=CO_2Me$)

(Annalen, 1929, **474**, 65 ; 1930, **478**, 54, 284; **480**, 197). This substance is prepared by reducing phæophorbide-*a* to a leuco-compound by means of hydriodic and acetic acids, followed by aerial oxidation. The whole process is an isomeric change, involving the reduction of the vinyl group on C_2, followed by the removal of the two " extra " hydrogen atoms on C_5 and C_6. *Phæoporphyrin-a_5* easily loses its carbomethoxyl group by ketonic fission to yield *phylloerythrin* (XV, $R=H$).

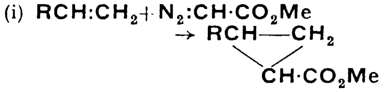


XV.

This substance (Marchlewski, Z. physiol. Chem. 1929, **185**, 8) is also formed by the biological degradation of chlorophyll, and can be isolated from the fæces of ruminants. Its structure has been established by Fischer by analytical methods (Annalen, 1931, **485**, 1 ; **486**, 107) and by synthesis (*ibid.* **490**, 91 ; 1932, **494**, 86 ; **497**, 181).

(3) The reasons for placing the phytyl group in the propionic acid side-chain, (C_7), and hence the methyl group on the carboxyl adjacent to C_γ are given by Conant and Hyde (J. Amer. Chem. Soc. 1929, **51**, 3668; 1931, **53**, 2382, *cf.* Fischer, Süs, and Klebs, Annalen, 1931, **490**, 38).

(4) The substituent group on C_2 in chlorophyll and the phorbides is vinyl (and not ethyl, as in the corresponding porphyrins). It reacts additively (i) with diazoacetic ester (Fischer and Medick, Annalen, 1935, **517**, 245) and (ii) with cold hydriodic acid in a stream of oxygen (" oxo-reaction," Fischer and Riedmair, Annalen, 1933, **505**, 87). The vinyl groups of the phorbides undergo the following changes in these reactions:



$$\text{(ii) } RCH{:}CH_2 + HI \rightarrow RCHI{\cdot}CH_3 \rightarrow RCH(OH)CH_3 \; \Big\downarrow \text{aerial oxidation} \; RCO{\cdot}CH_3$$

The Phase Test (Molisch.)—This is a colour reaction given by both forms of chlorophyll, and by derivatives such as the phorbides, phyllides, and chlorin-*e*, in which the dihydroporphin (phorbin) arrangement is maintained. It is not given by porphyrins. An ethereal solution of chlorophyll or a derivative is shaken with methyl alcoholic potash. The colour changes from green to bright yellow-brown and then back to green. The reaction is essentially an aerial oxidation, consuming two equivalents of oxygen (Steele, J. Amer. Chem. Soc. 1931, **53**, 3171). A similar reaction occurs when an alcoholic solution of chlorophyll is evaporated to dryness or allowed to stand in contact with air. The chlorophyll is said to be *allomerised* and loses its power of crystallisation (Willstätter and Utzinger, Annalen, 1911, **382**, 129). This was first recognised as an oxidation by Conant *et al.* (J. Amer. Chem. Soc. 1931, **53**, 359, 2382). The products formed in these reactions have been studied by Conant and by Fischer, but their chemistry is complex (*cf.* Chem. Soc. Annual Rep. 1935, **32**, 385).

Partial Synthesis of Chlorophyll.—As has already been mentioned, Fischer and his co-workers have synthesised phylloerythrin, (XV, $R=H$). For a complete synthesis of chlorophyll it is necessary (i) to convert this into phæoporphyrin-a_5 (XV, $R=CO_2Me$) ; (ii) to isomerise this to phæophorbide-*a*; (iii) to introduce the phytyl group into the side chain on C_7 ; and (iv) to introduce the central magnesium atom into the phæophytin so formed. The last two stages have been achieved by Fischer *et al.* (Annalen, 1934, **510**, 156 ; 1935, **519**, 244) ; the remainder of the synthetic problem awaits solution.

Chlorophyll-b.—This differs from chlorophyll-*a* in possessing an aldehyde group in place of methyl on C_3 (formula XIV), but the structure has not been conclusively established.

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[1] The position of the two additional hydrogen atoms, placed at C_5 and C_6 above, cannot as yet be regarded as certain. For a possible alternative, *see* Chem. Soc. Annual Rep. 1935, **32**, 392. Fischer proposes to distinguish these dihydro derivatives, in which hydrogen atoms are added to the porphin nucleus, by the general term *phorbin* (Annalen, 1936, **524**, 222).

[2] The suffix -*a* implies the preparation from a derivative of chlorophyll-*a* ; the 5 refers to the number of oxygen atoms in the molecule.

Bibliography.—R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Berlin, 1913 ; H. Fischer in Oppenheimer's "Handbuch der Biochemie," 1923, p. 351 ; 1930, 87 ; 1933, 262 ; J.C.S. 1934, 245 ; R. P. Linstead, Chem. Soc. Annual Rep. 1935, **32**, 362 ; 1937, **34**, 375 ; for the occurrence of substances of the chlorophyll series in organic minerals, *see* A. Treibs, Angew. Chem. 1936, **49**, 682.

R. P. L.

CHLOROPHYLLASE is an enzyme of the esterase class discovered by Willstätter and Stoll (Annalen, 1910, **378**, 18 ; 1911, **380**, 148), which in ethyl alcoholic solution splits off phytol from chlorophyll, forming ethyl chlorophyllide. The enzyme is widely distributed in leaves. It remains in the leaf residues after the chlorophyll has been extracted with alcohol. The method of preparation has been improved by Noack (Biochem. Z. 1927, **183**, 135). It is inactivated in the leaf powder by dialysis, but restored by the addition of $CaCl_2$.

E. F. A.

CHLOROPRENE *v.* BUTADIENES AND POLYOLEFINS (CONJUGATED).

CHLOROXYL. Cinchophen hydrochloride. Quinophan hydrochloride. Cinchophen is 2-phenylquinoline-4-carboxylic acid,

$$C_6H_5{\cdot}C_9H_5N{\cdot}COOH$$

(*Eli Lilly, London*), B.P.C.

CHLOROXYLONINE, $C_{22}H_{23}O_7N$, an alkaloid occurring in East Indian satinwood (Fr. *bois satiné*) (*Chloroxylon swietenia* DC : Rutaceæ). It crystallises from EtOH in colourless prisms, m.p. 182°–183°, $[\alpha]_D^{18}$ −9° 18′ (in chloroform), is soluble in excess of ammonia solution and is neutral to litmus. The salts are crystalline and dissociate in H_2O ; aurichloride, $B{\cdot}HCl{\cdot}AuCl_3$, groups of reddish-yellow needles, m.p. 70°. Chloroxylonine contains four methoxyl but no hydroxyl groups (Auld, J.C.S. 1909, **95**, 964). It produces dermatitis when applied to the skin and is the cause of this trouble sometimes experienced by satinwood workers (Cash, Brit. Med. J. 1911, Oct. 7, and Bull Imp. Inst. 1911, **9**, 351).

G. B.

CHLORPICRIN or CHLOROPICRIN. (Trichloronitromethane), $CCl_3{\cdot}NO_2$, is formed by the action of *aqua regia* on many organic compounds, *e.g.* cymene, styrene, etc. (Datta and Fernandes J. Amer. Chem. Soc. 1916, **38**, 1813), on acetone or the by-products of the acetone industry (Boyd, J.S.C.I. 1925, **44**T, 222), and by the action of nitric acid alone on many aliphatic chloro compounds such as chloral and chloroform (Dănăilă and Soare, Bul. Soc. Romăna Stiint, 1932, **35**, 53). It is most readily prepared by the action of chlorinating and oxidising agents on organic nitro compounds ; thus Green and Rowe obtained chloropicrin by treating nitro-*p*-phenylenediamine, dinitraniline, nitro-acetyl-*p*-phenylenediamine, etc., with sodium hypochlorite. The oxidation of picric acid or its salts with chlorine and basic materials to yield chloropicrin forms the subject of many patents differing chiefly in the nature of the basic constituent which may be a metallic oxide, carbonate, or borate (B.P. 142878), lime (U.S.P. 1413198 ; *see also* Frahm, Rec. trav. chim. 1931, **50**, 1125), or bleaching powder (U.S.P. 1327714, 1996388), etc.

Chloropicrin is a mobile oil, m.p. −69°C., b.p. 112°C., of great chemical activity, solutions in organic solvents often depositing ammonium chloride in the light (Piutti, Gazzetta, 1921, **51**, i, 145) or yielding other products by photochemical reaction (Alexejewski, Chem. Zentr. 1933, I, 3683). Reducing agents readily attack chloropicrin, iron and hydrochloric acid giving a theoretical yield of methylamine (Frankland *et al.*, J.C.S. 1919, **115**, 159) while mercaptans are reduced with formation of disulphides (Nekrassow and Melnikow, Ber. 1929, **62**, [B], 2091). Grignard reagents effect replacement of the three chlorine atoms by alkyl or aryl radicals accompanied by luminescence (Wedland, Z. Physik, 1906, **4**, 417 ; Asling and Dufford, Physical Rev. 1933, [2], **44**, 315).

Chloropicrin is best recognised by the colour reaction with dimethylaniline paper or by the formation of nitrite on reduction with metallic calcium (Alexejewski, J. Chem. Ind. Russ. 1931, **8**, 50). Quantitative determination in the atmosphere is effected either by absorption in acetic acid and reduction with iron, or by thermal decomposition over potassium carbonate at 350°, the chlorine in both methods being estimated gravimetrically (Deckert, Z. Hyg. 1929, **109**, 485).

Chloropicrin is highly poisonous (toleration limit for man, 60 cu.mm. per cu.m. air (Flury, Z. ges. exp. Med. 1921, **13**, 567), causing lachrymation, coughing, vomiting and eventually death by overwhelming edema of the lungs. It has a corrosive action on the skin and frequently produces abscesses (Underhill, Arch. Int. Med. 1919, **23**, 753), exposure of wounds, cuts, etc., to its action invariably producing ulceration.

The lethal properties of chloropicrin have led to its wide use as a disinfectant (F.P. 677340), preservative (Plücker, Z. Unters. Lebensm. 1932, **63**, 313), insecticide, fungicide, fumigant, etc. Its ready detection recommends it as a warning agent in illuminating gas (G. P. 447655) and in hydrogen cyanide (Zentr. Gewerbehyg. u. Unfallverhütung, 1927, **14**, [3], 65 ; U.S.P. 1949466). It has found many other uses, among which may be mentioned its use in veterinary practice (Chem. Rep. U.S. Dept. Agr. 1924, 12), the purification of vaccines (F.P. 612075), and the extermination of rats, foxes and other pests (Compt. rend. Acad. Agric. France, 1921, **7**, 568). Among purely chemical uses may be mentioned its employment in the manufacture of crystal violet (U.S.P. 1402195) and as an oxidising agent in the synthesis of quinoline and derivatives (B.P. 198462). Chloropicrin has been used in gas warfare and is regarded as the typical gas of the non-persistent deadly type (*v.* CHEMICAL WARFARE).

Literature.—Review of important work up to and including 1931, Jackson, Chem. Rev. 1934, **14**, 251. Complete summary 1848–1932, United States, Dept. of Agric., Miscellaneous Publications, No. 176.

CHLORQUINOL, 2-chloro-1:4-dihydroscybenzene, m.p. 106°, b.p. 263°.

CHLORYLEN. A brand of trichlorethylene. Used as an antineuralgic (*Schering, London*). B.P.C.

CHOCOLATE, from the Mexican word "Chocolatl," is the term applied to certain types of cocoa preparations intended for human consumption, either in the form of a beverage or as a confection. No legal standards have been adopted in the United Kingdom, although proposals to this effect have been made (*e.g.* R. Whymper, Congress of Cocoa and Chocolate Makers, Berne, 1911, and N. P. Booth, Seventh International Congress of Applied Chemistry, 1909). The majority of chocolate preparations contain sugar, but some, usually prepared for special purposes, are unsweetened or have saccharin as the sweetening agent. Those to be consumed in the form of beverage often contain a certain proportion, about 20%, of arrowroot or some other farinaceous substance. They may be in block form or as finely ground powder. The larger proportion of chocolate, however, is in the form of confectionery and this also falls into well-defined classes.

Manufacture.—The most simple type is what is usually known as plain chocolate, consisting essentially of cocoa and sugar. The cocoa, in the form of block cocoa from fermented beans (*see* COCOA), is first prepared by grinding in a mill between granite or steel rollers at a temperature (approximately 35°–40°C.) sufficiently high to melt the cocoa butter present and to reduce the whole to liquid form. In order to give a product which is smooth to the taste, the particles of fat-free cocoa must be ground as finely as possible. Mason (Analyst, 1933, **58**, 440) states that in well-known proprietary brands the maximum length of the particles varied from 1 to 200μ. The sugar used in the manufacture of good class chocolate consists of white high-grade crystals, while in lower quality chocolates an inferior grade is sometimes used. It should be dried and ground to a fine powder and may, with advantage, be warmed previously to admixture, in order to maintain the temperature of the mass. In special cases where sugar is inadmissible, as in chocolate intended for use by diabetic subjects, the sugar is replaced by saccharin. It is then usual, in order to give the necessary body to the chocolate, to add some form of meal or flour (preferably leguminous) and pea, bean, or linseed meal are preferred for this purpose. Flavourings, chiefly vanilla, but less frequently cinnamon, cloves, mace, nutmeg or their essential oils, are almost invariably added, usually in alcoholic solution. In the cheap forms of plain chocolate substances are used which many regard as adulterants. Chief among these are wheat or potato flour, rice, arrowroot, dextrin and ground cocoa shell. Milk chocolate is prepared by including in the molten mass a certain quantity of dried milk powder. Although, of course, the proportions used by different makers vary greatly, the following may be regarded as a typical composition : 15% fat-free cocoa matter, 25% cocoa butter, 40% sugar, and 20% milk powder. Nuts, chiefly hazel or almond, are often incorporated in plain or milk chocolate, to give nut chocolate and nut milk chocolate. All these forms of confectionery chocolate are run, whilst still in a molten condition, into moulds, giving, on cooling, bars, blocks, cakes and numerous fancy shapes.

Many types of chocolate confectionery are manufactured and sold, in which the chocolate forms an envelope or covering for other substances such as creams, biscuits, dried fruits, nuts, fruit jelly, liqueurs, and medicinal preparations such as pills. The most important of these fancy preparations are the creams. The interior cream is made either of powdered sugar or a mixture of this with glucose, with or without flavouring and colouring materials. The mixture is heated until it melts and, while in the liquid state, is poured into starch moulds of the desired shape on a table which can be agitated by mechanical means. On cooling, the creams set into a stiff granular mass. They are then coated with the hot liquid chocolate paste. In order to render the paste more mobile when heated and to give smoothness to the finished article, additional fat is added to the chocolate. This may be either cocoa butter or a substitute fat such as illipé. The covering is effected either by dipping the creams in the paste or by pouring the latter over the creams, uniformity being increased by means of the rocking table. In recent years machinery has been devised, and is now in use, to carry out the covering process.

Chemical Examination.—The chemical examination of chocolate follows well-defined lines, the principal features being the extraction, determination, and examination of the fat, the determination of the percentage of sugar, and a microscopical examination of the fat-free residue which will indicate the necessity for the determination, if present, of cocoa shell or farinaceous matter. In the case of chocolate-covered goods the covering and interior are separated, the proportions determined, and the two parts then examined independently.

Owing to the extensive use of substitutes for cocoa butter the complete extraction of the fat, not only for the determination of the proportion, but also for its subsequent examination, is a matter of considerable importance. The Soxhlet method, using light petroleum as a solvent, takes considerable time, and various methods have been suggested, for all of which rapidity, without loss of accuracy, is claimed. Bloomberg suggests extraction for 4 hours with anhydrous ether. In support of this, Finche (Bull. Off. intern. fabr. choc. 1932, **2**, 327) states that, if there is a possibility of a substitute fat being present, ether is preferable to light petroleum, as the latter will not dissolve out the wax which is likely to be present in the adulterant fat. Lepper and Waterman (J. Assoc. Off. Agric. Chem. 1925, **8**, 705), however, state that preliminary drying is necessary and, further, that the method is inaccurate owing to the extraction of theobromine and other substances. They suggest a method of exhausting the sample by several extractions with light petroleum, collecting the extract in a tared Erlenmeyer flask, and evaporating the solvent, drying, and weighing in the usual manner. Hughes (Chem. News, 1919, **119**, 104) suggests that the sample should be subjected to two preliminary washings with 50% alcohol, the mixture being centrifuged and the liquid decanted off. The process is then repeated several times with a mixture of equal volumes of ether and light petroleum, the successive ethereal layers being decanted off into a tared flask, the solvents evaporated and the fat dried and weighed. In order to avoid the evaporation of the solvent and the weighing of the dried residue, Hasse and Bake (Chem.-Ztg. 1923, **47**, 557) suggest the extraction of the fat by a mixture of equal volumes of ether and methyl ethyl ether. The difference between the respective refractometer readings of the solution and of the solvent is referred to tables which give the appropriate percentage of fat. Ruffy (Mitt. Lebensm. Hyg. 1926, **17**, 75) has attempted, with some slight modification, to apply the Gerber method of estimating fat in milk, cheese and meat. The presence of sugar in the chocolate presents a complication on account of its carbonisation by the sulphuric acid. It is claimed that this has been overcome by treating 3·5 g. of the chocolate with 20 ml. of ether in a strong walled tube. The mixture is well shaken and centrifuged ; 10 ml. of the clear liquid can then be transferred by a pipette to a butyrometer containing 13 ml. of sulphuric acid (density 1·5). This is shaken vigorously, centrifuged for 5 minutes, and the reading taken. Härtel and Jaeger (Z. Nahr.-Genussm. 1922, **44**, 291) suggest that the total fat should be extracted from milk chocolate with light petroleum and its Reichert-Meissl value determined. This value, multiplied by the percentage of fat and divided by thirty, gives the proportion of milk fat, which is taken to be one-quarter of the whole milk solids. In a later communication, however, Härtel (*ibid.* 1924, **48**, 32) states that if a certain kind of milk powder has been used, it is impossible to obtain all the fat by extraction with ether or light petroleum. In considering the fat extracted from milk chocolate, the possibility that skimmed milk has been used should not be ignored. The butyric and saponification numbers afford a reliable and rapid indication of this.

The proportion of sugar present can readily be determined by the polarimeter, after clarifying the solution with basic lead acetate. For accuracy in this method von Fellenberg and Ruffy (Mitt. Lebensm. Hyg. 1932, **23**, 6) state that certain precautions, which they describe, are essential, owing to the disturbing effect of the fat-free cocoa matter. Macara and Hinton (Congrès. Intern. Fabr. Chocolat. et Cacao, 1930, 341) have made an extensive investigation of the subject and evaluated the various known methods for plain and for milk chocolate. The examination of the latter presents special difficulty, owing to the varying and uncertain character of the milk used in manufacture. Härtel and Jaeger (*l.c.*) give a method in which the amount of milk solids is determined from the content of milk fat (*v. supra*). Whilst the determination of the lactose must be made on the original substance, the proportion of casein can be determined by treating the fat-free dry residue with sodium carbonate, as described in the paper. This is elaborated by Beythien and Pannwitz (Z. Nahr.-Genussm. 1923, **46**, 223) who state that the ratio of casein to lactose in twenty milk chocolates varied from 1·16 to 2·74. A method of determination of the milk content of chocolate, based upon the proportion of CaO in the ash, is suggested by Grossfeld (*ibid.* 1922, **44**, 240).

The presence of lecithin in cocoa and its preparations is of technical, and therefore of chemical, importance. Although the reason is not clear, the presence of lecithin promotes the mobility of hot cocoa or chocolate mass, but this is not so marked when milk has been added. Nottbohm and Mayer (Z. Unters. Lebensm. 1933, **65**, 55) have stated that free lecithin is absent from cacao beans but that choline from phosphatides, other than lecithin, may occur in the alcoholic extract, possibly produced by the action of the hot alcohol or by the roasting process. It is generally accepted, however, that some lecithin is present in the cocoa mass in varying proportions under 1%. The proportion is sometimes increased by the addition of commercial lecithin, thus making possible the extraction of an additional 5% of fat without loss of mobility in the hot mass. Various methods for the determination of lecithin have been proposed, one being the Soxhlet extraction with alcohol, the solvent being evaporated off and the residue treated with 30% H_2O_2 and sulphuric acid. The solution is then neutralised with ammonia and the phosphate from the lecithin precipitated with a mixture of strychnine nitrate and ammonium molybdate. The precipitate is filtered, dried and weighed. Winkler and Sale (J. Assoc. Off. Agric. Chem. 1931, **14**, 537) after extracting with alcohol and light petroleum, take up the dried extract with chloroform, add alcoholic potash, and evaporate again to dryness. The residue is then taken up in nitric acid and the P_2O_5 determined. Avent and Morgan (J.S.C.I. 1932, **51**, 169) consider that the best solvent to use in the extraction is a mixture consisting of four parts of benzene and one of alcohol.

If the microscopic examination of the fat-free residue indicates the presence of foreign starch or shell, the former can be estimated by the ordinary diastase method, allowance being made in the calculation of the result for approximately 14% of starch in the fat-free cocoa material, although it is better to make an independent determination of this value. The proportion of shell can be estimated by determination of the crude fibre, allowing for 6·10% in the fat-free rib and 18·25% in the fat-free shell, although in this case also an independent determination of the standards is to be advised. Offutt (J. Assoc. Off. Agric. Chem. 1932, **15**, 546) suggests certain modifications which render the fibre method applicable to milk chocolate. Jensen (" The Chemistry, Flavouring and Manufacture of Chocolate Confectionery and Cocoa ") quite properly emphasises the point that the fibre determination alone is probably only positive when over 25% of shell is present. A more decisive analytical interpretation may be placed upon the ratio of the nitrogen to fibre which differs very considerably for nib and husk; fibre/nitrogen for the former being 0·98–1·27, average 1·2, and for the latter 5·3–6·0, average 5·6.

The dietetic value of chocolate has often been emphasised and has been the subject of considerable discussion. Knapp ("Cocoa and Chocolate," 1920), quoting from the Journal of the Royal Agricultural Society of 1914, states that the "food value" of the cacao bean is represented by 183 units as compared with turnips 8, carrots 12, potatoes 26, rice 102, wheat 106, peas 113, and oatmeal 117. He also quotes the United States Department of Agriculture to the effect that the fuel value in lb.-calories of cocoa (0·5 oz. to 1 pint of water) is 65 compared with tea (0·5 oz. per pint) 15, and coffee (1·0 oz. per pint) 16. The figures represent the products without milk or sugar. He states that 1 pint of cocoa made of one-third milk, ½ oz. of cocoa, and 1 oz. of sugar would have a fuel value of 320 calories, and is therefore equivalent, in this respect, to ¼ lb. of beef or 4 eggs. Knapp further quotes data showing that eating chocolate has 2,538 calories per lb. compared with sugar 1,815, oatmeal 1,811, bread 1,180, beef steak 960, eggs 594, milk 314, potatoes 302, apples 214, and cod fish 209. Sasaki and Wakayama (J. Agric. Chem. Soc. Japan, 1932, **8**, 160) found that plain chocolate contained antineuritic vitamin B, 3 g. of chocolate per day being enough to cure antineuritic vitamin deficiency in pigeons. Jensen (*l.c.*), however, considers that the vitamin content of ordinary plain chocolate is unimportant, but the consumption of good class milk chocolate ensures valuable calcium and phosphorus assimilation by the definite vitamin D activity. Vitamin A is also present in proportion which increases the food value of milk chocolate.

F. G. H. T.

CHOCOLATE FATS (Confectionery Fats). Under this name may be grouped those fats which are employed in the manufacture of chocolate and confectionery, for which purposes a non-greasy, digestible fat, which displays a peculiar hard and brittle consistency ("snap") together with a relatively low melting-point (not over 37°–38°C.) is required. This particular combination of properties is well exemplified by **cacao-butter** (*q.v.*), which is both the typical and most-prized fat of this class, and is employed for the highest grades of chocolate, etc.; but for cheaper products, cacao butter may be replaced, either wholly or in part, by cheaper substitutes. Animal fats, which were used in earlier days, are liable to impart an unpleasant "animal flavour" to the chocolate, and at present only edible fats of vegetable origin are employed. Among the most important of these are Borneo (illipé) tallow (*q.v.*) (which, apart from its faintly greenish colour, closely resembles cacao butter in physical properties, and forms an excellent substitute) and the refined and deodorised "stearins" prepared from coconut and palm-kernel oils by removing the softer portions of the fat by expression; in addition, babassu and murumuru fats (*v.* COCONUT OIL GROUP) and sometimes shea fat and other "vegetable butters" or "green butters" are used, and, more recently, hydrogenated coconut and palm-kernel oils; the latter are harder than the corresponding natural fats, and are also claimed to assist in the prevention of "sugar-bloom" of chocolates. The use of hydrogenated oils, such as arachis, cottonseed or sunflower-seed oils, of appropriate melting-point has been proposed, but as a rule the texture of such products is not satisfactory. The use of Dika fat (*q.v.*, from the seed kernels of species of *Irvingia*), which possesses a suitable melting-point and "snap" has also been suggested from time to time (*cf.* Baudon, Bull. Mat. Grasses, 1926, **10**, 38).

It may be noted that the definitions for chocolate products adopted (the English delegation dissenting) by the International Congress of Manufacturers of Cocoa and Chocolate at Antwerp (1930) intentionally imply a prohibition of the use in "chocolate" of fats other than expressed cacao butter: the veto also extends to the use of solvent-extracted cacao fat or the fat from the germs and shell of the cacao bean. Similar standards have been adopted or are under consideration in the food legislation of many countries, including Austria, Belgium, Germany, Italy, the United States, Switzerland, France, New Zealand and South Africa, which in general forbids the undeclared inclusion in chocolate products of all fats other than expressed cacao butter (apart, of course, from the incidental introduction of milk fat or nut-fats associated with the corresponding ingredients of milk or nut chocolates). The Imperial Economic Committee in its Report on "Cocoa" (22nd Rept. 88/503/22, 1932, H.M.S.O.) has recommended that analogous legislation forbidding the use of more than a small proportion of cacao butter substitutes in the manufacture of chocolate pastes, etc., should be enacted in the British Empire; the provision of a small margin for other fats is suggested in accordance with the amendment of the English delegates to the Antwerp Congress, in order to allow the non-fraudulent inclusion of wholesome materials which might genuinely improve the product. Up to the present (1938) no legislative steps have been taken to implement the Committee's recommendations in the United Kingdom, where the chocolate manufacturers regard such regulations as undesirable.

E. L.

***allo*CHOLANIC ACID** *v.* CARDIAC GLYCOSIDES (Vol. II., p. 383*a*).

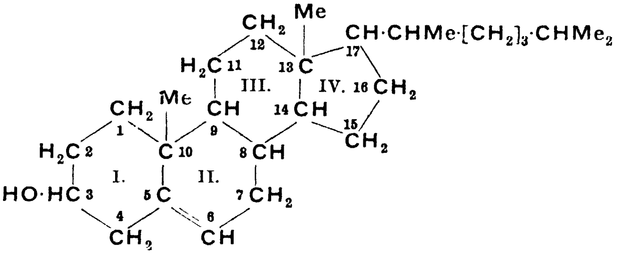
CHOLELYSE. A preparation of oleic acid for cholelithiasis (carbon).

CHOLESTEROL is a member of a group of naturally occurring unsaturated secondary alcohols, containing a nucleus of four reduced rings. The presence of some one of these sterols seems to be essential to the life of all cells, but as yet little is known as to the part they play in metabolism. In the tissues of animals, with the exception of certain invertebrates, cholesterol is present and appears to be synthesised *in vivo*. *Sitosterol* and *stigmasterol* occur in plant cells and the highly unsaturated *ergosterol* is a characteristic of many fungi (*e.g.* yeast, ergot, moulds).

In 1775, cholesterol was discovered by Conradi in gall-stones, of which it forms the chief constituent. It occurs either free or as its fatty acid esters in all animal tissues; brain and nerve tissue, suprarenal glands and egg yolk are particularly rich in it. It is readily extracted from gallstones ; it may be prepared by grinding up sheep's brain or other animal raw material with sand and plaster of Paris, or the minced tissue may be dried at 100°, ground in a coffee mill and the mass extracted with ether or acetone. The residue from the extract, after removing the solvent, is saponified with alcoholic potash, the alcohol distilled off and the cholesterol separated by extraction with ether. The formation of emulsions may be largely avoided by saponifying the ether extract of the tissue with an alcoholic solution of sodium ethoxide at ordinary temperature. After filtering off the compact mass of soaps which separates, the cholesterol crystallises out on concentrating the alcohol-ether filtrate.

Properties.—Cholesterol is insoluble in water, sparingly soluble in cold, easily in boiling alcohol (sp.gr. 0·87), and in $CHCl_3$, ether, CS_2, less soluble in acetone, petroleum, benzene and glacial acetic acid. It is soluble in fats, fatty acids, and in solutions of bile salts. It crystallises from ether or $CHCl_3$ in silky needles, m.p. 150° (corr.), from 90% alcohol it forms characteristic plates, containing one molecule water of crystallisation. Sp.gr. 1·046 ; optically active; $[\alpha]_D$ −31·12° in ether solution, −36·61° in $CHCl_3$. Sublimes unchanged at 200°, but is decomposed at higher temperatures, hydrogen being evolved at 300°–320°. Distils unchanged *in vacuo.*

Constitution.—Our knowledge of the structure of cholesterol is based on a long series of researches initiated by Mauthner in 1893 and carried out by, amongst others, Diels, Borsche, and especially by Windaus and his co-workers from 1903–1932. The formula which now finds general acceptance is a modification by Wieland and Dane (Z. physiol. Chem. 1932, **210**, 268) of that advanced by Rosenheim and King (Chem. and Ind. 1932, **51**, 464, 954).



The connection with the bile acids first suggested by Lifschutz (Ber. 1914, **47**, 1459) was definitely established by Windaus and Neukirchen (Ber. 1919, **52**, [B], 1915) ; the researches of Wieland and his colleagues on the structure of the bile acids have led to the identification of a series of degradation products, common both to cholesterol and the bile acids, which has been of the greatest importance in establishing their constitutions. The similarity of the structure of these substances with that of the group of sexual hormones is also of physiological importance.

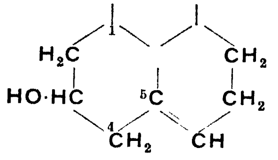
Hydrogenation.—Reduction with platinum and hydrogen gives *cholestanol* (dihydrocholesterol), m.p. 142° (Willstätter and Mayer, Ber. 1908, **41**, 2199), of which *coprostanol* (coprosterol) occurring in the intestines is an isomeride (Dorée and Gardner, J.C.S. 1908, **93**, 1625). Reduction with nickel and hydrogen at 200° gave a mixture of dihydroderivatives, δ- and ε-cholestanols; δ-cholestanol on boiling with amyl alcohol and sodium amyl oxide gave coprosterol, separated as the digitonide and recovered from this by boiling in xylene (Windaus, Ber. 1916, **49**, 1724). δ- and ε-Cholestanols were shown to be the isomeric forms of cholestanol and coprostanol respectively which depend on the inversion of the OH group. Neither δ- nor ε-cholestanol gives a precipitate with digitonin and they should now be known as *epi*cholestanol and *epi*coprostanol respectively.

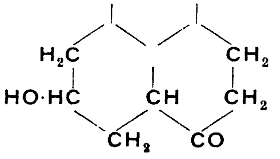
Oxidation.—Various oxidising agents, *e.g.* nitric and chromic acids, have produced a long series of oxidation products some of which are referred to below. By the action of ozone an ozonide containing 7 atoms O is formed (Dorée and Gardner, J.C.S. 1908, **93**, 1328; 1909, **95**, 638; 1916, **109**, 46).

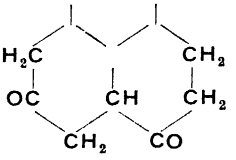
The Presence of a Secondary Alcohol Group was proved since the ketone *cholestenone* (m.p. 78°) was formed by oxidation with CuO at 300° (Diels and Abderhalden, Ber. 1904, **37**, 3092) or by oxidation of cholesteryl bromide with chromic acid in acetic solution at 70° (Windaus, Ber. 1906, **36**, 518) and removal of the Br by zinc and acetic acid ; in the latter reaction Tschesche has shown that the ethenoid link in cholestenone has moved from the 5:6 to the 4:5 position.

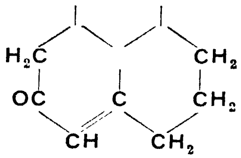
The Position of the Ethenoid and Secondary Alcohol Groups.—Originally Windaus postulated the presence of a terminal vinyl group ; if, however, cholesterol is oxidised with fuming nitric acid (Windaus, Ber. 1903, **36**, 3752; 1917, **50**, 133) and the unsaturated nitro-derivative obtained treated with zinc and acetic acid, nitrogen is removed as ammonia and the keto-alcohol, *cholestanonol*, $C_{27}H_{16}O_2$ (m.p. 140°), is formed, which on further oxidation with chromic acid gives *cholestanedione* (m.p. 170°–171°); this may also be obtained by oxidising cholesterol with cold chromic acid or KOBr solution to *cholestantriol*, oxidising further to *cholestanonediol*, splitting off water and reducing the cholestenedione thus formed (Windaus and Kirchner, Ber. 1920, **53**, [B], 614).

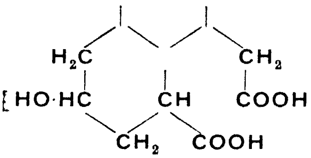
If cholestanonol is converted to the corresponding chloroketone, the latter on oxidation and reduction yields a C_{27} dibasic acid which on further oxidation is converted to a tetrabasic acid containing 27 C atoms, and which does not lose CO_2 on heating. The carbinol and ethenoid groups must therefore be in separate rings, and since no two carboxyl groups can be attached to the same carbon atom, the —CH:CH— and —CH·OH groups must also be separated by at least two carbon atoms (Windaus and von Staden, Ber. 1921, **54**, [B], 1059).

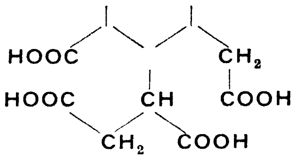

Cholesterol.


Cholestanonol.

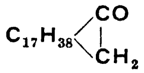

Cholestanedione.


Cholestenone.


Dibasic acid, $C_{27}H_{46}O_5$.

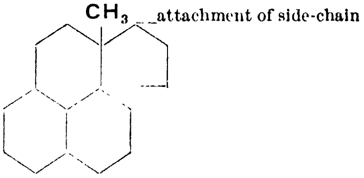

Tetrabasic acid, $C_{27}H_{44}O_8$.

Structure of the Side-chain.—Oxidation of cholesterol with nitric acid led to the isolation of a series of products amongst which Windaus (Z. physiol. Chem. 1918, **102**, 160; Windaus and Resau, Ber. 1913, **46**, 1246) identified dinitro*iso*propane, and acetic, succinic, methyl succinic, and α-glutaric acids, acetone, hydroxy*iso*butyric acid, methyl *iso*hexylketone and *iso*octane, each of which may be regarded as derived from an 8-carbon side-chain having the structure —CHMe·[CH$_2$]$_3$·CHMe$_2$. Since acetone and cholanic acid are formed by the oxidation of coprostane, which is known to contain the same side-chain as cholesterol, this structure for the side-chain was confirmed when Wieland, Jacobi, and Schlichting (Z. physiol. Chem. 1926, **161**, 80), by means of alternate Grignard condensations and oxidations, removed successive carbon atoms from the side-chain of cholanic acid until finally ætiocholanone,


$$C_{17}H_{38}\left\langle\begin{array}{l}CO\\ |\\ CH_2\end{array}\right.$$

(m.p. 105°), was left, the ketone group being present in ring IV, to which the side-chain was attached.

Ring Structure of the Nucleus.—Up to 1931 the presence of two reduced rings had been established in the cholesterol molecule. Dihydrocholesterol on oxidation gave the dibasic acid $C_{27}H_{46}O_4$, which on heating lost CO_2 and water, giving a cyclic ketone, $C_{26}H_{44}O$, and this on further oxidation gave a C_{26}-dibasic acid, which lost water on heating, forming a cyclic anhydride. To ring I, therefore, by Blanc's rule a cyclohexane structure was assigned (Windaus and Dalmer, Ber. 1919, **52**, [B], 162). When cholestene, containing the unsaturated link in Ring II, was converted through its nitro-derivative to a ketone and the latter oxidised, the dibasic acid produced was converted to an anhydride and by applying Blanc's rule that a 6-carbon chain dibasic acid (*e.g.* adipic) on heating gives a cyclic ketone and a 5-carbon dibasic acid (*e.g.* glutaric), an anhydride, a 5-carbon ring structure was attributed to Ring II. The same reasoning led to a 5-carbon ring structure being later attributed to Ring IV. The applicability of the Blanc rule to the determination of ring structure was criticised by Rosenheim and King (Chem. and Ind. 1932, **51**, 464) and on other grounds a 6-carbon ring structure is now attributed to both Rings I and II. Evidence that Rings III and IV are present in the nucleus of cholesterol was supplied by the work of Wieland and his colleagues on the bile acids (*q.v.*). By bacterial reduction of cholesterol in the intestines, coprosterol, isomeric with dihydrocholesterol, is formed. This gives on reduction pseudocholestane (isomeric with cholestane) which on oxidation yields a cholanic acid identical with that obtained from the cholic acid of bile. The three hydroxyl groups of the latter may be reduced giving $C_{24}H_{40}O_2$, cholanic acid. The saturated hydrocarbon, cholestane, $C_{27}H_{48}$, obtained by complete reduction of cholesterol (Mauthner, Monatsh. 1907, **28**, 1113; 1909, **30**, 635) yields on oxidation acetone and crystalline cholanic acid, $C_{24}H_{40}O_2$ (Windaus and Neukirchen, Ber. 1919, **52**, [B], 1915) isomeric with bile cholanic acid. The empirical formula $C_{27}H_{48}$ for the saturated hydrocarbons cholestane and coprostane, itself indicated the presence of a 4-ring system (Diels and Linn, Ber. 1908, **41**, 544). Further knowledge as to the structure of the skeleton of the sterol nucleus was supplied by the work of Diels *et al.* (Ber. 1927, **60**, [B], 140; Annalen, 1927, **459**, 1) on the dehydrogenation products of cholesterol and cholic acid. Mauthner and Suida (Monatsheft. 1896, **17**, 29) obtained as thermal decomposition products of cholesteryl chloride, a mixture of hydrocarbons of the formula $C_{19}H_{28}$, which no longer contained the 8-carbon side-chain of cholesterol; from the dehydrogenation products of this compound by hydrogen and selenium at 240°–310°, Diels isolated chrysene. Cholesterol similarly treated gave chrysene and two hydrocarbons, $C_{18}H_{16}$ and $C_{25}H_{24}$. The presence of four rings in the nucleus was therefore established. The hydrocarbon $C_{18}H_{16}$ was identified by Rosenheim and King and by Kon as 3-methylcyclopentenophenanthrene. In chrysene, the **Me** group at position 13 in cholesterol has entered the 5-carbon ring IV forming a 6-carbon ring. $C_{25}H_{24}$ was identified as a pentacyclic hydrocarbon, formed by ring closure between the terminal side-chain and the nucleus, thus giving evidence as to the position of attachment of the side-chain. The grouping



must, therefore, be present in the cholesterol molecule.

When it had been established that the nucleus contained 17 **C** atoms, the side-chain 8 **C** atoms, 2 **C** atoms remain to be accounted for. Evidence has been given above that a methyl group occurs at position 13, and the other methyl group is placed at position 10 for the following reasons, when ring 1 of the cholesterol molecule was broken down step by step to a monobasic acid by the action of Grignard's reagent this acid was very difficult to esterify indicating that a tertiary carbon atom containing a methyl group was probably adjacent to the **COOH** group. For this and other reasons position 10 has been assigned to the second methyl group.

X-ray examination of the sterols by Bernal (Chem. and Ind. 1932, **51**, 466) showed that the previously accepted formulæ did not accord with the crystallographic measurements, whereas Rosenheim and King's formula (*ibid.* 464) is supported both by the crystallographic measurements and the optical evidence.

Isomerism in the Cholesterol Series.—A large number of isomeric derivatives exist. Structural isomerides arise from variation in the position of the double bond. Stereoisomerides due to the inversion of the **OH** group occur and may be differentiated by the action of digitonin, those containing the **OH** group in the same position as cholesterol being precipitated by digitonin, no such precipitate being formed when the **OH** group is in the inverted position. Stereoisomerism due to the relative position of Rings I and II also takes place. Thus cholesterol and cholestene may be converted to coprosterol and coprostene by the action of **HCl**. Cholestane and its derivatives are regarded as the *trans*-derivatives; the coprostane series as the *cis*-compounds. Windaus (Ber. 1904, **37**, 4753) prepared isomeric oxyketodibasic acids, $C_{27}H_{42}O_6$, one forming a lactonic acid (m.p. 192°–193°) which on heating with potash gave an oxyketo acid incapable of lactonisation (*trans* form), and concluded that the reduced ring structure must be capable of *cis-trans* isomerism.

Nomenclature.—Considerable confusion exists in the nomenclature of the cholesterol derivatives since names were given before the relationships of the various compounds had been elucidated. It has been suggested by Rosenheim and King (Chem. and Ind. 1934, **53**, 91) that certain useful simplifications showing structural connections should now be made. The term pseudo has been used to denote both steric and structural isomerism; it seems desirable now to use the term "epi" for all substances formed by steric inversion of the **OH** group, *e.g.* epicholestanol, epicoprostanol, these substances do not give insoluble digitonides. The term copro should be given to the *cis*- derivatives related to coprosterol; some of the changes involved would be:

Old nomenclature. (*Cis*- derivatives.)	New nomenclature. (*Cis*- derivatives.)
Coprosterol (saturated alcohol)	Coprostanol
Allocholesterol (unsaturated alcohol)	Coprostenol
Coprostanone	Coprostanone
Coprostenone	Coprostenone
Pseudocholestane	Coprostane
Pseudocholestene	Cholestene

Cholesteryl Esters.—Those of the lower fatty acids are prepared by heating cholesterol with the anhydrides of the acids; those of the higher fatty acids by boiling the cholesterol with the acid and a dehydrating agent. These substances on melting form anisotropic liquids, many of the esters having three stable liquid phases. The *acetate* melts at 114°, the *propionate* at 98°. The *benzoate* melts at 144°–145° to a turbid liquid which examined with the polariscope shows definite crystal structure and at 178° passes to a clear liquid, the p-*nitrobenzoate* melts at 189°, p-*aminobenzoate* at 238°. The *laurate* can be heated several degrees above its melting-point without melting (Shriner and Ko, J. Biol. Chem. 1928, **80**, 1).

Detection.—Cholesterol crystallises in characteristic thin rhombic plates from 90% alcohol. Under the microscope they often show notched angles and exhibit a curious overlapping arrangement. A number of colour tests are given by the unsaturated sterols; the most important for cholesterol is Salkowski's test, in which 2 c.c. of a $CHCl_3$ solution of cholesterol are shaken with an equal volume of conc. H_2SO_4, the $CHCl_3$ ayer passes through blood-red and cherry-red to purple, which lasts for several days; poured into a basin, it becomes successively blue, green and yellow owing to absorption of water. The sulphuric acid layer is strongly fluorescent.

Iodine Value.—This may be satisfactorily determined by Hübl's method if the conditions are closely defined; Wijs reagent gives variable and much too high results, owing either to substitution or, according to Schoenheimer, because re-formation of the double bond takes place with liberation of iodine (J. Biol. Chem. 1935, **110,** 461). The resin acids also give abnormally high values with Wijs solution. The anthracene hydrocarbons react similarly with Hübl and Wijs reagents, whereas the phenanthrenes give much higher values with Wijs than with the Hübl solution (Smedley-MacLean and Thomas, Biochem. J. 1921, **15,** 321). Dam recommends a solution of bromine and pyridine sulphate (8 g. Br, 10 g. conc. H_2SO_4, and 8 g. pyridine per litre) (Biochem. Z. 1924, **152,** 101).

Estimation.—The total amount of cholesterol in a tissue may be determined by precipitating the alcoholic solution of the unsaponifiable fraction with a 1% solution of digitonin in 90% alcohol; after standing for some hours, the precipitate, containing 25% cholesterol, is collected on a Gooch filter, washed with alcohol and ether, dried at 100°, and weighed. If it is desired to estimate separately the free and combined cholesterol, the alcoholic solution of the ether-soluble extract must first be precipitated with the digitonin solution and the residue then saponified and the cholesterol estimated in the unsaponifiable fraction. Prescher (Z. Nahr.-Genussm. 1917, **33,** 481) recommends that after saponification the soap should be decomposed with hydrochloric acid, and the chloroform solution of the fatty acids separated, filtered and treated with the digitonin solution at 50°, the liquid being stirred during the precipitation. A micro method for the estimation of cholesterol by oxidation of the digitonide is described by Okey (J. Biol. Chem. 1930, **88,** 367). In fats where adulteration with vegetable oils has taken place, it is important to discriminate between the vegetable and animal sterols; for this the acetates or dibromides must be prepared and their melting-points examined.

Marcusson and Schilling recommend the following method (Chem.-Ztg. 1913, **37,** 1001): 50 g. fat are shaken for 15 minutes in a separating funnel with 20 c.c. 1% alcoholic solution of digitonin. The bottom layer of oil is run off, the alcoholic upper layer containing the flocculent precipitate of digitonide is shaken with 50 to 100 c.c. ether. The precipitate is washed with ether, dried, powdered, again washed, and then heated with 1·5 c.c. acetic anhydride in a test tube for half an hour. On cooling, cholesterol and sitosterol acetates crystallise out. The m.p. of the recrystallised acetates are respectively 114° and 128°. Cholesterol and sitosterol may also be separated by crystallising their dibromides from ether and glacial acetic acid (Windaus, Chem.-Ztg. 1906, **30,** 1011). A mixture of 4 g. cholesterol and 4 g. sitosterol is dissolved in 80 c.c. ether and 80 c.c. 5% bromine in glacial acetic added. After standing for one hour at 0°, the precipitate is washed with 40 c.c. glacial acetic acid, and with 40 c.c. 50% acetic acid, the washings being added to the filtrate and a further precipitate added to the original precipitate, which is then washed with water and dried. The precipitate contains the cholesterol dibromide, the filtrate the sitosterol compound. The cholesterol is recovered by heating the precipitate with 100 c.c. glacial acetic and 5 g. Zn dust for 2 hours, the excess of zinc filtered off, and a large quantity of water added. The sitosterol is obtained by treating similarly the solution of the sitosterol dibromide.

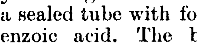
Cholesterol occurs with other sterols in a preparation of wool fat known as lanolin and used mainly for medicinal purposes; owing to the ease with which, when mixed with olive oil, it is absorbed by the skin, it is used in the preparation of ointments and salves; it is also used in the manufacture of cosmetics and pomades and for softening leather. Wool fat, which contains about 70% sterol and 30% fatty acids, is saponified by caustic soda giving an emulsion which on dilution with water gives the so-called wool-milk. On centrifuging impure lanoline separates out and is purified by repeatedly kneading with water and centrifuging. The purified product is afterwards kneaded with 30% water and forms the hydrous wool fat of the B.P. Anhydrous lanolin absorbs about 100% of water, does not become rancid, and is antiseptic. A commercial preparation of cholesterol extracted from the spinal cord of cattle is also available.

*iso**Cholesterol*, m.p. 137°–138°, $[\alpha]_D = +60°$, also occurs in wool fat and may be separated from cholesterol by heating the mixed sterols for 30 hours in a sealed tube with four times their weight of benzoic acid. The benzoates are insoluble in boiling alcohol and are separated by crystallising from ether. Cholesteryl benzoate crystallises in shining plates, *iso*cholesterol benzoate as a light powder, m.p. 190°–191°. *iso*Cholesterol gives no colour reaction with chloroform and sulphuric acid and is not precipitated by digitonin. When shaken with sulphuric acid, the yellow solution gradually changes to brownish red; in the Liebermann-Burchard test, a brown-red colour is obtained Windaus and Tschesche (Z. physiol. Chem. 1930, **190,** 58) showed that *iso*cholesterol is a mixture of two sterols both containing 30 carbon atoms.

	Alcohol. m.p.	Acetate. m.p.	Benzoate. m.p.
Agnosterol, $C_{30}H_{48}O$	162°	173°–174°	203°
Lanosterol, $C_{30}H_{50}O$	140°–141°	113°–114°	191°

I. S. M.

CHOLESTEROPHAN. Dimethyl parabanic acid,



CHOLIC ACID, $C_{24}H_{40}O_5$, 3:7:12-trihydroxycholanic acid (*v.* BILE ACIDS).

CHOLINE AND RELATED SUBSTANCES. *Choline, trimethyl - β - hydroxyethylammonium hydroxide,*

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3{\cdot}OH,$$

is formed by the hydrolysis of lecithin and hence probably occurs in combination in all living cells; its isolation from animal and vegetable tissues has been recorded very many times, but has no significance, since it is readily set free from phosphatides by chemical processes or by enzyme action. Kauffmann (Z. physiol. Chem. 1911, **74**, 175) has shown that when perfectly fresh ox brain is worked up rapidly, with suitable precautions, hydrolysis may be avoided and no choline is obtained. The free choline in semen is the result of enzyme action (Kahane and Levy, Compt. rend. 1936, **202**, 2186). The best natural source is crude lecithin ; hard egg-yolk is extracted with ether and then with alcohol ; the extracts are mixed and evaporated and the residue is boiled for 1 hour with 50 parts of cold saturated baryta solution. After removal of the baryta as carbonate or sulphate, the filtrate is evaporated and the residue is extracted with absolute alcohol. Alcoholic mercuric chloride then precipitates choline mercurichloride, $C_5H_{14}ONCl{\cdot}6HgCl_2,H_2O$, which salt can be crystallised from hot water ; it is very slightly soluble in the cold. After removal of the mercury by hydrogen sulphide and evaporation of the filtrate, choline chloride is extracted from the residue by alcohol. For the isolation of small quantities of choline, along with betaine, from plants, *see* Schulze (Z. physiol. Chem. 1909, **60**, 155). The final separation depends on the ready solubility of choline chloride in absolute alcohol, which leaves betaine chloride behind. Choline is, however, best prepared synthetically, by the method of Renshaw (J. Amer. Chem. Soc. 1910, **32**, 128) ; rather more than one equivalent of trimethylamine gas is passed into ethylene chlorohydrin in a tube cooled to −12° to −20°, which is subsequently heated to 80°–90°; the yield is almost quantitative. (For another method, starting from ethylene dibromide, *see* Krüger and Bergell, Ber. 1903, **36**, 2901.)

Choline can be recognised to some extent qualitatively by means of its dichroitic crystalline *periodide* (Florence's test for semen ; Bocarius, Z. physiol. Chem. 1901, **34**, 339 ; Rosenheim, J. Physiol. 1905–1906, **33**, 220). This salt is precipitated at a concentration of choline of 10^{-6} by adding a concentrated solution of iodine in potassium iodide. If the choline solution contains sodium bicarbonate, the weak base betaine is not precipitated, and can be separated as periodide after acidification of the filtrate from the corresponding choline salt (Stanĕk, Z. physiol. Chem. 1905, **46**, 280 ; 1906, **47**, 83 ; **48**, 334). The *reineckate* of choline, $[Cr(SCN)_4(NH_3)_2]NMe_3C_2H_4{\cdot}OH$, with a solubility of 10^{-5} may also be employed qualitatively and quantitatively. The *mercurichloride* mentioned above forms crossed hexagonal prisms, m.p. 249°–251°, soluble in 50 parts of water at room temperature, but practically insoluble in absolute alcohol. The *platinichloride*, $(C_5H_{14}ON)_2PtCl_6$, dissolves in 5·8 parts of water at 21° and is dimorphous ; the conversion of the regular isotropic into the anisotropic monoclinic form is the surest means of identifying choline without analysis (Kauffmann and Vorländer, Ber. 1910, **43**, 2735). The *aurichloride* dissolves in 75 parts of water at 21° and in hot alcohol. Neither the gold nor the platinum salt has a characteristic melting-point. The free base and many of its salts are syrupy (for details, *see* Gulewitsch, Z. physiol. Chem. 1898, **24**, 513). For soluble non-deliquescent salts, *see* G.P. 290523, 290740. Minute quantities of choline can be recognised and estimated by physiological means, after conversion into acetylcholine (Guggenheim and Löffler, Biochem. Z. 1916, **74**, 208 ; Führer, *ibid.* 1916, **77**, 408).

Acetylcholine, $HO{\cdot}NMe_3{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$, has during the last decade come to be recognised as a substance of great physiological importance. Its powerful action in lowering the blood pressure (many thousand times as great as that of choline) was noticed by Hunt and de Taveau in 1911 (U.S. Hyg. Labor. Bull. 73). It was first recognised in ergot by Dale (J. Physiol. 1914, **48**, 3) and isolated by Ewins (Biochem. J. 1914, **8**, 44). Dale and Dudley (J. Physiol. 1929, **68**, 97) isolated it from the spleen of horses, in which tissue physiological tests indicated the presence of 10 mg. per kg. Bischoff, Grab and Kapfhammer (Z. physiol. Chem. 1930, **191**, 179 ; 1931, **199**, 135 ; **200**, 153) claim to have isolated 28 mg. per litre from ox blood by means of Reinecke salt, but this relatively enormous yield has not been confirmed by others. Acetylcholine is secreted by the endings of the parasympathetic nerves, when the nerves are stimulated, and so acetylcholine is responsible for the humoral transmission of certain nervous impulses ; thus it passes into the fluid perfusing a frog's heart, when the vagus nerve is stimulated, and the fluid can then affect a second heart (Loewi). In these experiments the amount of acetylcholine is too small to be isolated, but its presence may be inferred from its rapid hydrolysis and inactivation by boiling, by alkali, or by an enzyme. This enzyme, *choline-esterase*, was isolated from horse serum by Stedman, Stedman and Easson (Biochem. J. 1932, **26**, 2056) ; its action is inhibited by physostigmine and similarly constituted synthetic urethanes. Hence physostigmine poisoning is in reality a poisoning by the subject's own acetylcholine. The synthesis of acetylcholine in ox brain has recently been demonstrated by Stedman and Stedman (Biochem. J. 1937, **31**, 817) ; they isolated 18 mg. as the double chloroplatinate of choline and acetylcholine from minced ox brains, after 2 hours incubation at 37° ; physiological tests (on leech muscle) indicated that 48 mg. had been formed. The last-named paper and one by Dudley (Biochem. J. 1929, **23**, 1064) should be consulted for the difficult technique of isolating this very unstable ester in the presence of much larger quantities of choline.

A large number of other esters of choline and its homologues have been investigated (Hunt and de Taveau, *l.c.* ; Menge, J. Biol. Chem. 1911, **10**, 399 ; U.S. Hyg. Labor. Bull 96 ; Ewins, Biochem. J. 1914, **8**, 366 ; Fourneau and Page, Bull. Soc. chim. 1914, [iv], **15**, 544). They are all less active than the acetyl derivative, to which the *pyruvyl* ester perhaps comes nearest. The *nitrous acid ester*, formed by oxidising choline with nitric acid, was long regarded as "synthetic" muscarine and considered to be an aldehyde, until Ewins (Biochem. J. 1914, **8**, 209) showed its true nature. *Muscarine* of *Amanita muscaria*, the Fly Agaric, has a pharmacological action related to that of acetylcholine and, according to Kögl, Duisberg and Erxleben (Annalen, 1931, **489**, 156) probably the constitution

$$HO{\cdot}NMe_3{\cdot}CH(CHO)CHEt{\cdot}OH.$$

The alkaloid *sinapin* in black mustard seeds is the choline ester of sinapic acid. In connection with the physiological action of snake venom, Fourneau and Page (*l.c.*) found *palmityl-* and *stearyl- choline* to be strongly hæmolytic. Acetylcholine and some related derivatives have been used tentatively in therapeutics ; the most important of these is perhaps *carbaminoylcholine* (*Doryl* of E. Merck). Other substances in which choline is esterified with phosphoric acid have been isolated from animal tissues (liver) ; they seem to result from the partial hydrolysis of lecithin and sphyngomyelin ; for these and the biochemistry of choline, *see* Kahane (Bull. Soc. Chim. biol. 1937, **19**, 207).

Other bases related to choline are *neurine* or *vinyltrimethylammonium hydroxide*,

$$CH_2{:}CH{\cdot}NMe_3{\cdot}OH,$$

formed from choline by putrefaction and having a similar physiological action, but 10–20 times as toxic. *β-Aminoethyl alcohol* or *β-hydroxyethylamine* (*colamine*), $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, was obtained by Thudichum in 1884 by the hydrolysis of the brain phosphatide kephalin (*i.e.* lecithin without *N*-methyl groups). Colamine has also been obtained from other phosphatides (Trier, Z. physiol. Chem. 1913, **86**, 1, 141, 153, 407). For a fuller account of choline and related substances, *see* Guggenheim, "Die biogenen Amine," 2nd ed., Berlin, 1924 (3rd ed. in preparation), and for the biochemistry of choline, Kahane, Bull. Soc. Chim. biol. 1937, **19**, 205.

G. B.

CHOLINE ESTERASE is an enzyme of the lipase class which hydrolyses acetylcholine, $HO{\cdot}NMe_3{\cdot}CH_2{\cdot}CH{\cdot}OAc$ (*v.* CHOLINE). In view of the outstanding importance of acetylcholine as the substance by means of which the parasympathetic nerves produce their effect, the existence in the body of an enzyme capable of destroying it is of interest.

It is apparently a specific enzyme and widely distributed in the tissues (Galehr and Plattner, Pflüger's Archiv. 1927, **218**, 488, 506). A method of preparing it from blood serum is described by Stedman and Stedman (Biochem. J. 1935, **29**, 2563). Its activity is best determined by titration with 0·02 *N*-$NaOH$ with bromothymol blue as indicator (Stedman, Stedman and White, Biochem. J. 1933, **27**, 1055). It is destroyed by heat above 56°.

It acts on other esters of choline ; an increase in the size of the acyl group increases the rate of hydrolysis unless a side chain has been introduced, when a decrease occurs (Easson and Stedman, Proc. Roy. Soc. 1936, B. **121**, 142).

The order is *n*-butyryl$>$propionyl$>$*iso*butyryl $>$acetyl$>$benzoyl.

The influence of p_H on choline esterase to some extent depends on the substrate : the optimum lies above p_H 8·0. The enzyme is remarkable in being reversibly and specifically poisoned by a group of synthetic urethanes allied to eserine, particularly physostigmine and miotine. Easson and Stedman (*l.c.*), who have most recently studied the question, assume that the substances which inhibit the enzyme act by combining with it in the same way as the choline esters and thus blocking the active groups. In this connection an interesting calculation has been made in regard to the activity of the enzyme, namely, that each *active group* in it hydrolyses about 1,490 mols. of acetylcholine per second. The amount of inhibitor required to produce a large inhibition of the enzyme is very minute.

E. F. A.

CHOLUM or **CHOLAM** *v.* CEREALS,. MILLET.

CHONDRIN. An albuminous substance allied to and resembling gelatin, obtained by boiling cartilage with water. It dries to a hard, horny substance which softens to a jelly in cold water, and is soluble in boiling water. An aqueous solution is decomposed by 2% aluminium hydroxide into chondroitin sulphuric acid (*v.* CHONDROITIN) which remains in solution and has $[\alpha]_D$ −46·59° and the chondrin residue ($[\alpha]_D$ −386·85°) which is adsorbed in the colloid ; this reaction affords a method of differentiating between chondrin and glutin, as a solution of the latter gives an immediate precipitate with barium chloride, whilst a solution of chondrin gives no appreciable precipitate, but if the solution is stirred with 10% aluminium hydroxide and filtered, the filtrate gives with barium chloride an immediate precipitate of the barium salt of chondroitin sulphuric acid (Rakuzin and Braudo, J. Russ. Phys. Chem. Soc. 1926, **52**, 397 ; Z. Unters. Lebensm. 1926, 52, 397 ; Rakuzin, Chem.-Ztg. 1923, **47**, 602).

CHONDODENDRINE, CHONDODRINE, an *iso*quinoline alkaloid.

CHONDROITIN is a tetrasaccharide consisting of two glucuronic acid and two chondrosamine units.

E. F. A.

CHONDROSAMINE is 2-aminogalactose. It has been obtained from some of the mucins and mucoids and has been investigated by Levene and La Forge (J. Biol. Chem. 1914, **18**, 123 ; 1915, **20**, 443).

E. F. A.

CHOPIN EXTENSIMETER *v.* BREAD (Vol. II, p. 78*b*).

CHOPPING NUT or **ESERÉ NUT** *v.* CALABAR BEAN (Vol. II, p. 198*d*).

CHROMATOGRAPHY *v.* CAROTENOIDS (Vol. II. p. 398) and CHEMICAL ANALYSIS (*ibid.*, p. 628).

CHROMITE or **CHROME-IRON-ORE.** A member of the spinel group of minerals, consisting essentially of ferrous oxide and chromic oxide, $FeO{\cdot}Cr_2O_3$ or $FeCr_2O_4$, analogous to the aluminates. The ferrous oxide is, however, often partly replaced by magnesia, and the chromic oxide by alumina, so that there is a passage to chrome-spinel or picotite ; on the other hand, with a replacement of chromic oxide by ferric oxide, there may be a transition to magnetite (Fe_3O_4 or $FeFe_2O_4$). All these minerals are cubic in crystallisation and belong to the same isomorphous group—the spinel group. The actual amount of chromic oxide varies considerably, as shown by the following analyses ; the ordinary ore, as mined, contains on an average 45% Cr_2O_3.

	Cr_2O_3	Al_2O_3	Fe_2O_3	FeO	MgO
I.	67·9	—	—	32·1	—
II.	44·15	22·41	5·78	11·76	15·67
III.	59·20	7·15	n.d.	25·02	4·42
IV.	41·23	24·58	2·28	16·99	14·77
V.	56·54	12·13	—	18·01	14·08

I. Calculated for $FeCr_2O_4$.
II. Franklin, Macon Co., North Carolina.
III. Price's Creek, Yancey Co., North Carolina (J. H. Pratt, Amer. J. Sci. 1899, **7**, 281). Also SiO_2 2·80, MnO 0·69.
IV. Tampadel, Lower Silesia (H. Traube, Z. deut. Geol. Ges. 1894, **46**, 50).
V. Dun Mountain, New Zealand.
(For analyses of chromite isolated from meteorites, *see* W. Tassin, Proc. U.S. Nat. Museum, 1908, **34**, 685.)

In general appearance, chrome-iron-ore is very like magnetite, but it is readily distinguished from this by the dark-brown colour of its streak or powder, and by the fact that it is only slightly, if at all, magnetic. Sp.gr. about 4·5. Crystals are of rare occurrence, the mineral being usually found as grains disseminated in basic rocks of igneous origin, especially those rich in olivine (viz. the peridotites). Sometimes these grains are segregated into nodular masses of considerable size and with a granular to compact texture. Rocks of this kind, when subjected to weathering processes, become hydrated and altered into serpentine, and for this reason most of the workable deposits of chrome-iron-ore are in serpentine rocks. With the denudation and breaking down of these rocks, the heavy grains of the chemically resisting chromite collect in the beds of streams and rivers ; and some of the deposits worked in the Ural Mountains are of this nature.

Chromite is the only commercial source of chromium and its compounds. It is used for the preparation of the oxides and chromates employed as pigments, and in dyeing, calico-printing and tanning ; in the manufacture of chrome-steel and ferrochrome, and for chrome-bricks and furnace linings. It is mined in Asia Minor, Serbia, Greece, the Ural Mountains, New Caledonia, India, Baluchistan, Rhodesia, Quebec, California and Oregon ; and formerly, to a considerable extent, at Bare Hills, near Baltimore in Maryland, and in Lancaster Co. in Pennsylvania. Quarries were, at one time, worked on Unst, one of the Shetland Isles (Special Reports on the Mineral Resources of Great Britain, Vol. 5, Mem. Geol. Survey, 1916).

References.—Chrome ore and chromium, Imperial Mineral Resources Bureau, London, 1920. On the chemical composition of chromite, *see* L. W. Fisher, Amer. Min. 1929, **14**, 341. On Canadian deposits, F. Cirkel, Dept. of Mines, Canada, No. 29, 1909 ; and those of Rhodesia, F. E. Keep, Bull. Geol. Survey Southern Rhodesia, 1930, **16**.

L. J. S.

Chromite as a Refractory Material.—Chromite is one of the most important neutral refractories, especially in metallurgical furnaces. It is said to have been used in France in 1872 and earlier in Austria. In addition to a high melting-point, in the neighbourhood of 1,950°C., it is not acted upon by siliceous fluxes, and for that reason is often placed as a "buffer" layer between the basic magnesia and acid Dinas brick in Siemens-Martin and other furnaces. On account of its resistance to gases, flue-dust and slag particles, chrome bricks are used for the ports of gas-fired furnaces, tap-holes, etc. It is employed for the construction of furnaces for the smelting of copper and nickel ores (Glenn, Eng. and Min. J. 1901, **72**, 637 ; J.S.C.I. 1902, **21**, 52), and is also very resistant to oxides of antimony, lead and bismuth.

Chromite should contain over 40% of chromic oxide and less than 6% of silica, the remainder being composed of ferrous oxide, alumina, lime, and magnesia. In some cases it is employed in the form of lumps or loose powder which can be packed in position and afterwards sintered or even fused into a monolithic layer. The material may also be ground, mixed with a suitable binder, moulded into bricks, which must be fired at a high temperature. It has been stated that clay could not be used as a binder, but chromite mixed with from 10 to 15% of Zettlitz kaolin gave a very refractory product (Simonis, Stahl u. Eisen, 1908, **28**, 334 ; J.S.C.I. 1908, **27**, 283). The most usual binders are refractory clays, bauxite, magnesite and lime, the last giving a highly refractory brick. Chromite bricks are heavy (sp.gr. about 4·5), close-textured and fairly strong mechanically, but, like magnesia bricks, fail suddenly at about 1,400°C. under a load of 50 lb. to the sq. in. Wologdine (Bull. Soc. d'Encour. 1909, **108**, i, 879 ; J.S.C.I. 1909, **28**, 709) gives the following figures for the heat conductivity :

Chromite I. . . .	0·0057	C.G.S. units.
„ II. . . .	0·0055	„
„ agglomerated	0·0028	„

The electrical resistivity at various temperatures has been measured by Hartmann, Sullivan and Allen (Trans. Electrochem. Soc. 1920, **38**, 279) and by McLeod and M'Mahon, working under Professor Stansfield at McGill University (*ibid.* 1912, **22**, 89). The two sets of measurements which differ somewhat are given in the following table :

	Hartmann *et. al.*	Stansfield *et. al.*
Cold . .	48·1 Megohms.	—
800°C. .	803 Ohms	2,800 Ohms per cm. cube
900°C. .	525 „	760 „ „
1,000°C. .	171 „	420 „ „
1,100°C. .	78 „	430 „ „
1,200°C. .	63 „	450 „ „
1,300°C. .	77 „	410 „ „
1,400°C. .	85 „	320 „ „
1,500°C. .	41 „	—

Chromite appears to expand regularly with increasing temperature and has a larger thermal expansion than any other ordinary refractory material, except magnesite, amounting to 1·6% at 1,500°C. (B. Bogitch, Compt. rend. 1921, **173**, 1358).

During the last few years, a considerable amount of attention has been given to the effect of relatively large admixtures of chromite with other refractory materials, especially chrome-silica, chrome-magnesite, and chrome-alumina mixtures. In some cases, possibly most marked with chrome-alumina mixtures, heating to a high temperature may bring about chemical reaction between the oxides with the formation of new compounds, but in others the chromite retains its identity. At the same time, its presence modifies the behaviour of the mixture in service. Thus, chrome-silica bricks are mechanically stronger at high temperatures than plain chrome bricks, and tend to spall less than either chrome or silica bricks. Similarly, chrome-magnesite bricks have a greater resistance to spalling than many fireclay bricks and a higher " refractoriness-under-load " than normal silica bricks (Budnikoff and Mandelgrin, Ber. Deut. keram. Ges. 1932, **13**, 521 ; Lynam and Rees, Trans. Ceram. Soc. 1936, **35**, 138 ; *ibid.* 1937, **36**, 110 *et seq.* ; Chesters and Lee, *ibid.* 1937, **36**, 294); Rieke and Ungewiss, Ber. Deut. Keram. Ges. 1935, **16**, 482).

The following analyses, taken from various sources, illustrate the composition of chromites for refractories :

Cr_2O_3 . . .	51·23	62·20	53·66
Fe_2O_3 . .	36·63	28·10	16·20
Al_2O_3 . .	3·17	2·60	13·90
MgO . . .	3·79	1·10	9·22
CaO . . .	5·10	3·07	0·78
SiO_2 . . .	1·87	2·60	5·20
	101·79	99·67	98·96

W. C. H.

CHROMIUM. Symbol **Cr**, at. wt. 52·01, at. no. 24, isotopes 50, 52, 53, 54. The common chromium mineral and the only important ore of chromium is *chromite*, $FeCr_2O_4$ (*q.v.*). Chromium also occurs in chrome diopside and in the mica known as fuchsite, which is distinguished from other varieties by its brilliant green colour, in chromium garnet and in certain chloritic chromium minerals which accompany the chromite. As lead chromate it occurs in *crocoisite*, $PbCrO_4$, and as basic lead chromate in the rare mineral *melanchroite* or *phœnicochroite* (formerly *phœnicite*) $3PbO\cdot 2CrO_3$. Meteorites often contain chromite but rarely more than 1%. The red colour of the ruby (Papish and O'Leary, Ind. Eng. Chem. [Anal.], 1931, **3**, 13), the greenish colour of serpentine, *verde antico* marble, emeralds and many other minerals are due to the presence of oxides of chromium (Sainte-Claire Deville and Carron, Ann. Chim. 1865, [iv.], **5**, 108; *cf.* Verneuil, Compt. rend. 1910, **150**, 185). Mitchell (Astrophys. J. 1930, **71**, 1) confirmed the presence of chromium lines in the solar spectrum. Spectrographic analysis has revealed the presence of traces of chromium in the ash of all the organs, somewhat more concentrated in the thyroid and spleen (Dutoit and Zbinden, Compt. rend. 1930, **190**, 172). Demarçay reported the presence of chromium in traces in wood ashes (*ibid.* 1900, **130**, 91).

Koenig (Landw. Jahrb. 1910, **39**, 775; J.C.S. 1911, **100**, ii, 524) described the stimulative and toxic effects of various chromium compounds on plants. The results obtained by other workers, that the higher the degree of oxidation of chromium the more toxic its effect, were confirmed, a wheat plant being killed by a 0·0064% solution of sodium dichromate, whereas it required a 0·5% solution of chromium sulphate to give a similar result. The red coloration given by sodium 1:8-dihydroxy-naphthalene-3:6-disulphonate was utilised for the identification of traces of chromium in plant ash. Workmen exposed to the dust of potassium dichromate have suffered from skin eruptions and inflammation of the septum of the nose. There is a risk of chromium poisoning in lithography, founding, tanning, and dyeing where chromium compounds are handled, and also from the spray from chromium-plating baths (Dobbs, J.S.C.I. 1930, **49**, 163T). The protection of workers has been studied by the Metropolitan Life Insurance Co. (Service Bur. Bull. No. 408; J. Amer. Leather Chem. Assoc. 1936, **31**, 110; *cf.* Feil, *ibid.* **31**, 65; Halle aux Cuirs, 1935, 149). Chromic salts are less toxic than chromates (Akatsuka and Fairhall, J. Ind. Hyg. 1934, **16**, 25; D. Brard, " Toxicologie du chrome," Paris, Hermann & Cie, 1935).

Chromium has many uses in the arts; it forms a series of alloys with iron, carbon, nickel, manganese, etc., which include the stainless steels ; it is deposited electrolytically as a bright coating which does not tarnish, in the process of chromium-plating. Chromic salts are used in tanning leather and for the preparation of chromium green. Chromates, usually sodium or potassium dichromate, are also employed in tanning, and to an important extent in wool dyeing and as chromated gelatin in photomechanical and colour printing. The alkali chromates are employed in the preparation of the pigments, lead chromate (chrome yellow), and zinc chromate (zinc yellow). In organic chemistry chromic acid is used as an oxidising agent; chromic oxide serves as a catalyst in the synthesis of methyl alcohol and in the cyclisation of hydrocarbons. *Cf.* Homer Adkins, " Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, 1937.

The scientific interest of chromium is considerable, the metal can assume a passive state, it forms many series of coloured compounds, corresponding to all the valencies from 2 to 6 inclusive. Cr^{II}. The blue solutions of chromous salts containing the ion Cr^{++} are powerful reducing agents. Cr^{III}. The chromic salts derived from Cr_2O_3 exist in two states, violet crystallisable solutions which on boiling become green and do not then crystallise. These solutions may contain unstable hydrated ions, *e.g.* $[CrCl\cdot 5H_2O]^{++}$. Cr^{VI}. The yellow chromates. and orange dichromates derived from the trioxide CrO_3 ionise in solution to CrO_4^{--} and $Cr_2O_7^{--}$. Cr^{IV}. Quadrivalent chromium is contained in the series of salts derived from triphenyl chromium hydroxide $(C_6H_5)_3CrOH$. Cr^{V}. The corresponding tetraphenyl chromium salts $(C_6H_5)_4CrX$ contain quinquevalent chromium. The chromohydrocarbons

$$(C_6H_5)_3Cr \text{ and } (C_6H_5)_4Cr$$

have been prepared in the free state. There are three series of perchromates, red M_3CrO_8, blue $MCrO_6$, and brown co-ordination compounds $[(NH_3)_3CrO_4]$. A very large number of chromammines and analogous substances containing pyridine, urea, etc., have been described. The ethylene diamine compound $[CrCl_2 \cdot 2en]Cl$ and also the double oxalate $K_3[Cr(C_2O_4)_3]$ have been separated into optically active forms. The resolution indicates an octahedral structure for these and other co-ordination compounds of chromium.

For a review including chromite, chromium, and ferrochrome, *see* Roush, Mineral Ind. 1936, 54, 61–69. The following statistics of the production of chromite ore during recent years have been supplied by the Imperial Institute in May, 1938.

World's Production of Chrome Ore.
(Long Tons.)

Country.	1930	1931	1932	1933	1934	1935	1936	1937
British Empire								
Southern Rhodesia .	202,385	80,334	15,445	34,493	70,961	104,240	180,499	271,265
Union of South Africa	13,508	22,967	19,065	33,541	60,388	89,003	172,896	165.958
India	50,684	19,913	17,865	15,526	21,576	39,127	49,486	62,307
Other British Empire	1,676	226	454	918	2,781	2,795	1,739	5,000
Foreign Countries								
Greece	23,032	5,545	1,531	14,550	30,209	29,309	46,599	55,061
U.S.S.R. (*a*) . . .	65,666	72,123	76,242	80,913	85,943	181,500	216,000	(*d*)
Yugoslavia . . .	50,583	57,462	38,524	25,833	46,604	51,540	53,190	58,918
Cuba	38,380	11,882	500	21,837	57,325	(*b*)42,081	69,257	(*c*)93,098
Japan	11,421	9,573	12,295	19,681	26,792	35,736	37,868	(*d*)
Turkey	27,750	24,987	—	74,189	117,951	148,096	161,292	189,468
New Caledonia . .	60,916	72,979	68,332	49,281	54,310	54,437	47,000	47,264
Philippine Islands .	—	—	—	—	—	(*b*)1,272	2,873	75,209
Other foreign countries . . .	1,827	3,589	603	3,544	1,133	840	4,364	5,644
Total . .	548,000	381,000	251,000	374,000	576,000	780,000	1,043,000	(*d*)

(*a*) Figures up to and including year 1934 refer to the year ending Sept. 30th ; figures for 1935 and 1963 refer to the calendar year and probably contain some ore needing concentration. (*b*) Exports. (*c*) Imports into the United States. (*d*) Not available.

For a discussion of chromite ore and chromium, world production, prices, and imports, *see* Anon. Mineral Ind. 1935, **44,** 58 ; *cf.* "Imperial Institute Monograph on Mineral Resources, Chromium Ore, new edition in preparation.

Pure Chromium.—Adcock (J. Iron and Steel Inst. 1927, **115,** 369, 435) obtained the metal of a high degree of purity by the electrolysis of a bath containing 300 g. chromic acid and 10 g. sulphuric acid per litre. A yield of 22·6 g. per kw.-hr. of compact metal was deposited on a rotating steel tube which formed the cathode. This chromium contained hydrogen which was removed by melting the product *in vacuo,* and oxygen which could only be eliminated by heating in a current of pure dry hydrogen at 1,500°–1,600°. The final product, although spectroscopically pure, was criticised in the discussion of the paper (*l.c.* 435). The difficulty of the preparation is shown by the fact that the product could not be melted even in alumina crucibles *in vacuo* without being contaminated with oxygen.

Many methods depend on the reduction of chromic oxide. Rohn (Z. Metallk. 1924, **16,** 275) heated the oxide to 1,500° in a Heraeus tube furnace in a stream of purified dried hydrogen. The best of these methods is probably the thermit process of H. Goldschmidt (Annalen, 1898, **301,** 19) in which a mixture of chromic oxide and granular aluminium is brought to exothermic reaction and fusion of the whole mass by firing it with a fuse made of barium peroxide and aluminium powder. The metal, 98–99% pure, separates from a layer of slag.

Commercial Chromium is made by one of two methods, the thermit process above described, and by reduction of chromic oxide with the theoretical proportion of silicon, to which some lime is added to form a slag, in an electric furnace. The chromium thus obtained is 98–99%, and may contain up to 0·9% Fe and not above 0·8% silicon as major impurities. The metal from the thermit process contains a maximum of 0·9% aluminium. Neither product contains more than 0·2% carbon (A. B. Kinzel and W. Crafts, "The Alloys of Iron and Chromium," vol. 1, 1937, McGraw-Hill Book Co. Inc., London and New York; Treitschke and Tamman, Z. anorg. Chem. 1907, **55,** 402).

Pyrophoric Chromium has been prepared by heating chromium amalgam, Hg_3Cr and $HgCr$, *in vacuo* below 300°. The amalgam is prepared electrolytically or by the action of sodium amalgam on solutions of chromic salts (Férée Compt. rend. 1895, **121,** 822).

Physical Properties.—Electrolytic chromium is a very hard bluish-white metal which takes a brilliant polish. The hardness is about 9 on Mohs scale, or 2,000 by the scratch test which gives 1,950 for case-hardened steel (U.S. Bureau of Mines, Information Circular, I.C. 6566, 1932). The presence of occluded hydrogen has been considered to be the cause of part at least of the hardness (Adcock, *l.c.*). According to Makarieva and Biryukov (Z. Elektrochem. 1935, **41**, 623) heating the metal to remove hydrogen may even increase the hardness. The face-centred cubic lattice structure of chromium confers maximum hardness, the hexagonal and body-centred cubic lattices being less hard and converted into the first-named structure on heating. The density of degassed electrolytic chromium at 25°/4° is 7·138±0·003 and at −50°/4° is 7·156±0·001 (Hüttig and Brodkorb, Z. anorg. Chem. 1925, **144**, 347). Döring found 7·085 for 98% chromium made by the thermit process (J. pr. Chem. 1902, [ii], **66**, 65). International Critical Tables, ii, 456, and also Landolt-Börnstein Tabellen, 1927, Ergänz. i, 104, give the density as 7·1, for later values, *v. ibid.* Ergänz. II, i, 210 ; III, i, 282. The coefficient of thermal expansion between 20° and 100° is 0·0000067 (Hidnert Phys. Rev. 1932, [2], **39**, 186).

Very divergent values have been published in the earlier literature for the melting-point of chromium, 1,420°–2,000°, figures which indicate the difficulty of preparing a pure specimen. L. Müller (Ann. Physik. 1930, [v], **7**, 48) determined the cooling curve of electrolytic chromium with a thermo-couple between 2,000° and 1,400° and found the m.p. 1,805°. F. Hoffmann and Tingwaldt (Z. Metallk. 1931, **23**, 31), employing an optical pyrometer, observed the m.p. of electrolytic chromium contained in a magnesia crucible in an evacuated resistance furnace, and also the melting temperature at a hole in a bar of sintered chromium powder heated by an electric current. The first method gave 1,800°±10° and the second 1,765±10°. Friemann and Sauerwald (Z. anorg. Chem. 1931, **203**, 73) found 1,915°–1,925° *in vacuo* and 1,650° in a mixture of H_2 and N_2. According to Greenwood (Proc. Roy. Soc. A, 1909, **82**, 396) the metal boils at about 2,200° ; it can be distilled in an electric furnace under ordinary pressure (Tiede and Birnbrauer, Z. anorg. Chem. 1914, **87**, 149) but a carbide distils in a graphite tube.

The specific heat at −252·5° is 0·014 (Dewar, Proc. Roy. Soc. A, 1913, **89**, 158), at −190° values near 0·08 were found by several observers (*inter alia* Richards and Jackson, Z. physikal. Chem. 1910, **70**, 414) ; average values at 0°, 0·104, and 100°, 0·110, have been recorded (Schimpff, *ibid.* 1910, **71**, 257 ; Schübel, Z. anorg. Chem. 1914, **87**, 81). At 1,000° Umino found 0·135 (Sci. Rep. Tôhokw, 1926, **15**, 597). According to Jaeger and Rosenbohm (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 489) thermal effects due to polymerisation may cause uncertainty in determining the specific heat of chromium at different temperatures.

The arc and spark spectra of chromium are complex, the most intense rays are Å $\underline{4254\cdot34}$, $\underline{3605\cdot33}$, 4274·80, 4289·73, 3578·68, and $\underline{3593\cdot49}$; the wavelengths underlined are the raies ultimes of de Gramont (*cf.* F. Twyman, " Wavelength Tables for Spectrum Analysis," 1923, A. Hilger, London).

H. von Wartenberg measured the refractive index *n* 2·97, the index of absorption $n\kappa$ 4·85, and the reflectivity R%, 69·7 for the yellow mercury line 579 $m\mu$ (Verh. Deut. Physikal. Ges. 1910, **12**, 105). According to Bernoulli (Physikal. Z. 1904, **5**, 632), active and passive chromium give different values for reflexion, a result which suggests the presence of a surface film on the passive metal.

Chromium forms a thermoelectric couple with nickel (Hase, Z. Metallk. 1929, **21**, 200). Since chromium functions only as anode, *e.g.* in an alcoholic solution of calcium nitrate, it will rectify an alternating current (Sborgi and Cappon, Nuovo Cim., 1922, [vi], **23**, 303).

Allotropes of Chromium.—The existence of two allotropes of chromium has been inferred from X-ray examination of the metal (Bradley and Ollard, Nature, 1926, **117**, 122). Three allotropes are reported by Sasaki and Sekito (Trans. Electrochem. Soc. 1931, **59**, 437 ; *cf.* Makarieva and Biryukow, *l.c.*). The hexagonal allotrope contained in electrolytic chromium is transformed into one of the two cubic modifications by heating the deposited metal to 130° for 15 minutes (Wood, Phil. Mag. 1937, [vii], **23**, 984).

Passive and Active Chromium.—Chromium is described as active when it dissolves in the halogen hydracids, oxalic, sulphuric, and hydrofluosilicic acids, or when the metal becomes charged with hydrogen while used as a cathode. A fresh surface exposed by scratching the passive metal is active. Chromium becomes passive when immersed in chlorine- or bromine-water, nitric, chromic and chloric acids, and in solutions of potassium permanganate, ferric chloride or potassium ferricyanide ; when exposed to air or oxygen or if employed as an anode provided the voltage exceeds a critical value. In the electrochemical series passive chromium is placed near Pt, whilst active chromium is close to Zn. Muthmann and Fraunberger measured the potentials acquired by a number of samples in KCl solution against a calomel electrode and found +0·35 volts with active chromium and −1·47 with passive chromium ; these are the extreme values (Sitzungsber. bayr. Akad. 1904, [ii], **34**, 201). Local patches of more or less active or passive metal may exist on the same specimen. The existence of an oxide film on passive chromium has been much discussed in the literature (*e.g.* W. J. Müller, Z. Elektrochem. 1931, **37**, 328. For protective oxide films on metals, *see* numerous papers by U. R. Evans). Among the authors who dispute this explanation are Rathert (Z. physikal. Chem. 1914, **86**, 567) and Bowman (Rec. trav. chim. 1924, **43**, 1, 399).

Müller and Essin (Z. Elektrochem. 1930, **36**, 963–972) measured the potential of chromium, deposited electrolytically on copper, in contact with solutions of different acids as a function of time and of temperature. The results indicate that at 0° the metal is passive towards *N*-hydrofluoric, -hydrochloric, -hydrobromic, -sulphuric, -perchloric, -phosphoric, and -nitric acids, but that on warming to a temperature which is characteristic for each acid and increases with the diameter of the anion, the metal becomes active towards the first four acids; in phosphoric, perchloric, and nitric acids it remains inactive at 100°.

Further experiments by Müller and Schwabe (Z. Elektrochem. 1931, **37**, 185–197) on the activation of chromium by cathodic polarisation in acid solutions show that each acid requires a definite activation potential. The negative potential at which activation occurs in normal acid solutions increases in the order, hydrochloric $<$ hydrofluoric $<$ hydrobromic $<$ sulphuric $<$ perchloric $<$ orthophosphoric; thus, activation is more easily affected the smaller the anion is. The potentials for electrolytic and thermit chromium are slightly different. When the activation is affected by grinding with an emery wheel there is again a definite activation potential, which depends on the anion of the acid, and the order is the same as that given above. The experiments lead to the following deductions concerning the nature of passivity. Chromium in the passive state is covered by a network of chromic oxide molecules, which are anchored to the units of the chromium space lattice. Acids cannot dissolve the oxide film except by penetrating between the molecules, and the size of the anion is therefore important.

In a later paper (Z. physikal. Chem. 1936, **176**, 273) E. Müller states that in $M\text{-}HCl$ at 20°, chromium amalgam oscillates periodically between the active and passive states. In $M\text{-}H_2SO_4$ massive chromium is passive, but can be rendered permanently active by weak cathodic polarisation. The experimental results in the paper are contrasted with the author's earlier explanation of passivity (Z. physikal. Chem. 1932, **159**, 68).

Chemical Properties.—The pure metal is not affected by air, oxygen, or chlorine at temperatures up to 300° C. It is not attacked by nitric acid, aqua regia, ammonia solution, acetic acid, lactic acid, or by molten zinc, tin, or brass. Chromium is attacked by gaseous hydrogen chloride, and at high temperatures by sulphur vapour and hydrogen sulphide. It dissolves in hydrochloric acid and the rate of evolution of hydrogen varies periodically with the time, a phenomenon which has been studied by several authors (Ostwald, Z. physikal. Chem. 1900, **35**, 33, 20; Adler, *ibid.* 1912, **80**, 385; E. S. Hedges and J. E. Myers, J.C.S. 1924, **125**, 604; "The Problem of Physico-Chemical Periodicity," London, 1926). Chromium is also dissolved by the other halogen hydracids, and by dilute sulphuric acid, the action being accelerated by heating, or by the presence of impurities in the metal. The metal burns with vivid sparks when heated in the oxyhydrogen blowpipe forming the sesquioxide, Cr_2O_3.

Electrolytic Chromium, Chromium Plating.—The brilliant appearance, the hardness and resistance to corrosion of electrolytically deposited chromium are available only since the existence of the modern art of chromium plating, a process which was not generally successful before Fink's U.S.P. 1581188 of 1926. Fink employed a bath containing 250 g. CrO_3 and 2·5 g. SO_4 ion per litre with a current density of 34 to 144 amp. per sq. ft. of cathode surface. More recently Piersol has used 350 g. CrO_3, 2–6 g. H_2SO_4, and 10 g. of H_3BO_3 per litre and obtained hard deposits with the bath at 57° and a rate of deposition of 0·002 in. per hour (Metal Clean. Finish. 1935, **7**, 325, 385, 535). With a bath resembling Fink's (*supra*), the hardness increased with falling temperature, 38° or over being too high (*ibid.* **7**, 73, 169; Kronsbein, J. Electrodep. Tech. Soc. 1935, 23; Cymboliste, Compt. rend. 1937, **204**, 1654). Poor results are obtained with baths of chromic salts (Applied Chemistry Reports, 1933, **18**, 363). Specifications for chromium coatings are discussed by Francis-Carter, J. Electrodep. Tech. Soc. 1935, **10**, 69. Explanations of the process of electrolysis of the three types of chromium compounds Cr^{++}, Cr^{+++}, and CrO_4^{--} are proposed by Kasper (Bur. Stand. J. Res. 1932, **9**, 353; 1933, **11**, 515; *cf.* Weiner, Z. Electrochem. 1936, **42**, 585; Rogers, Trans. Electrochem. Soc. 1935, **68**, 1; E. Müller, Z. Elektrochem. 1937, **43**, 361). Wright (Chem. and Ind. 1930, 473) distinguishes two types of chromium plating: (1) on a preliminary coating of nickel or copper for preventing rusting of automobile and machinery parts, taps, cutlery, and scientific instruments; (2) direct plating on tools, pressure rollers, and plates where a hard surface is required (*cf.* Gardam, Metal Ind. 1930, **36**, 245, 279; Dobbs, *ibid.* **36**, 435). The direct method is much less important (*cf.* Vignos, B, 1937, 798). Disadvantages of the chromic acid bath and suggested improvements are discussed by Cuthbertson (Applied Chemistry Reports, 1937, **22**, 413; heavy Ni and Cr plating in England, Fescol process, by Bonilla, Trans. Electrochem. Soc. 1936, **71**, Preprint 2, 9). Among special works, *see* "Chromium Plating," by Bauer, Arndt, and Krause, transl. E. W. Park, E. Arnold, London, 1935; B. Freeman and F. G. Hoppe, "Electroplating with Chromium, Copper, and Nickel," Prentice Hall, New York, 1930; R. Schneidewind, "Chromium Plating," University of Michigan, 1928.

Chromium Hydride.—Electrolytic chromium may contain 250 times its volume of hydrogen (Carveth and Curry, J. Physical Chem. 1905, **9**, 353). The gas contained in the metal burns off without further heating after the specimen is brought into contact with a flame (Hüttig and Brodkorb, Z. anorg. Chem. 1925, **144**, 341). When an ethereal solution of chromic chloride and phenyl-magnesium bromide is shaken with hydrogen gas, a black precipitate is formed of the composition CrH_3 (Weichselfelder and Thiede, Annalen, 1926, **447**, 75).

Chromium Carbonyls.—The hexacarbonyl is formed when carbon monoxide acts on Grignard reagents (*e.g.* $C_6H_5{\cdot}MgBr$) and chromic chloride in ether-benzene solution (Job and Cassal, Bull. Soc. chim. 1927, [iv], **41**, 1041). After hydrolysis the product is steam-distilled and $Cr(CO)_6$ is obtained by vacuum-sublimation as colourless, strongly refracting, orthorhombic crystals, isomorphous with $Mo(CO)_6$ and $W(CO)_6$, and readily soluble in inert organic solvents. It is so volatile that it disappears from a watch-glass in a few hours. It melts in a sealed tube at 149°–150° and the vapour decomposes slowly above 120°, yielding a mirror of pure Cr

(Hieber and Romberg, Z. anorg. Chem. 1935, **221**, 321). When heated with pyridine in a sealed tube under suitable conditions it yields bright red $Cr(CO)_3(C_5H_5N)_3$, yellowish-red $Cr_2(CO)_7(C_5H_5N)_5$, and yellow

$$Cr(CO)_4(C_5H_5N)_2$$

(Hieber and Mühlbauer, *ibid.* **221**, 337). For organo-metallic compounds of chromium, *see* J. Newton Friend, "Inorganic Chemistry," vol. xi, pt. 4, C. Griffin & Co., London, 1937 ; E. Krause and A. von Grosse, "Chemie der metall-organischen Verbindungen," Berlin, 1937.

Chromium Phosphate, prepared by mixing cold solutions of chrome alum and of disodium hydrogen phosphate is an amorphous violet precipitate which left in contact with the solution becomes crystalline and has the composition $CrPO_4,6H_2O$. On boiling with water it is converted into the green crystalline hydrate $CrPO_4,4H_2O$. A green amorphous hydrate of this composition is obtained by precipitating a hot chrome alum solution with excess of Na_2HPO_4. A dihydrate may be prepared by heating the hexahydrate in air, but at low redness an anhydrous black salt and at a higher temperature a green basic salt is obtained (Joseph and Rae, J.C.S. 1917, **111**, i, 196). Green pigments, known as *vert Arnaudon* and *vert Plessy*, have been prepared by reducing a solution of potassium dichromate and adding a solution of an acid phosphate (*cf.* Carnot, Compt. rend. 1882, **94**, 1313; Chrome Greens, this vol., p. 107*d*).

Chromium Sulphate, $Cr_2(SO_4)_3$, a crystalline red powder obtained by heating the hydrated salt above 325° *in vacuo* (Krauss, Querengässer, and Weyer, *infra*). It is insoluble in water (Friedrich and Blickle, Metallurgie, 1910, **7**, 323), as is the acid salt, $Cr_4H_2(SO_4)_7$ (Caley and Burford, Ind. Eng. Chem. [Anal.], 1936, **8**, 63). Series of violet and of green crystalline hydrates are known and also of green amorphous hydrates. Krauss, Querengässer, and Weyer (Z. anorg. Chem. 1929, **179**, 413) quote from the literature violet hydrated sulphates crystallising with 18, 17, 16, 15, 14, 12, 6, 5, 4 mols. of water, and green hydrated sulphates crystallising with 11, 8, 7, 6, 5 mols. Their paper describes the preparation of violet hydrates with 18, 9, and 3 H_2O, also of the green crystalline hydrate with $12H_2O$, and the green amorphous hydrate with $15H_2O$. The solution of this last salt is precipitated by $BaCl_2$ on boiling, but not in the cold. Cold solutions of the violet hydrates are completely precipitated by $BaCl_2$. The ordinary violet hydrate with $18H_2O$ is obtained by crystallising, or by adding alcohol to a solution of chromic hydrate in the calculated quantity of sulphuric acid. Its crystal water has also been reported as 17 mols. H_2O (*inter alia* Werner and Gubser, Ber. 1901, **34**, 1592; Montemartini and Vernazza, L'Ind. Chimica, 1933, **8**, 445). The violet solution begins to turn green at 65° and the change is complete on boiling. Alcohol now precipitates a green basic salt (Venable and Miller, J. Amer. Chem. Soc. 1898, **20**, 484). The green solution becomes violet on standing. According to Montemartini and Vernazza (L'Ind. Chimica, 1932, **7**, 1001), a solution of chromic sulphate at 32·5° contains 34·5% of the violet form, between the concentrations 3·5 and 7%, and equilibrium is established within 28 days from either side. Although hydrolysis no doubt occurs in the violet solution (Denham, Z. anorg. Chem. 1908, **57**, 361), the change of colour on boiling is probably due to the formation of green complex ions. These have been variously formulated to indicate the masked —SO_4 groups and the combined water. Zaldes (J. Gen. Chem. Russ. 1936, **6**, 1325; A.I, 1937) writes

$$(Cr(OH_2)_6]_2(SO_4)_3+H_2O \rightarrow$$
$$[Cr(H_2O)_4(SO_4)_2]+H^{\cdot}+[Cr(H_2O)_5OH]^{\cdot\cdot}+SO_4$$

Basic complexes in chromic sulphate solutions are considered to be effective in chrome tanning (J. A. Wilson, J. Amer. Leather Chem. Assoc. 1936, **31**, 165; *cf.* Stiasny *et al.*, Collegium, 1928, **49**, 72). The green crystalline sulphate, $Cr_2(SO_4)_3{\cdot}12H_2O$, is prepared by passing SO_2 into a concentrated CrO_3 solution at 0°–5° and crystallising *in vacuo* (Krauss *et al.*, *l.c.*). In a series of papers in the Comptes rendus from 1905 to 1907, Colson described the preparation of green hydrated sulphates with respectively 3, 2, and 1 masked SO_4 groups, the two latter salts being successive stages in the hydrolysis of the first, $[Cr_2(SO_4)_3]$. Recoura (Ann. Chim. 1895, [vii], **4**, 511) prepared the mono-, di-, and trichromosulphuric acids by heating a green crystalline hydrate, $Cr_2(SO_4)_3,8H_2O$, with 1, 2, or 3 mols. of sulphuric acid to 110°–120°. The acids are respectively di-, tetra-, and hexabasic, corresponding to the proposed formulæ $[Cr_2(SO_4)_4]H_2$, $[Cr_2(SO_4)_5]H_4$, and $[Cr_2(SO_4)_6]H_6$. They dissolve to deep green solutions in water which if freshly prepared do not give the reactions of Cr or SO_4 ions. According to Küntzel *et al.*, chromium sulphate complexes are contained in a boiled and cooled chromic sulphate solution. Masking of chromic salts occurs on adding a neutral salt containing an anion common to both (Collegium, 1935, 484). Montemartini and Vernazza (*l.c.* **8**, 445) prepared a saturated solution of chromic sulphate, $Cr_2(SO_4)_3,17H_2O$, at 18° containing 84·8% of this salt, and state that the equilibrium violet⇌green was not affected by addition of alkali sulphate, the percentage of violet salt in this solution was 51·68.

Chrome Alums.—The double sulphates of chromium and potassium or ammonium, $M_2SO_4,Cr_2(SO_4)_3,24H_2O$, are important chemicals; they crystallise in large violet octahedra and are very soluble in water. The corresponding sodium salt does not crystallise so readily. The ammonium salt is made by mixing molecular proportions of the constituent sulphates, potassium chrome alum is a common by-product from oxidations with potassium dichromate, although on the large scale, *e.g.* anthracene → anthraquinone, the chromic acid solution is regenerated by electrolytic oxidation of the chromic sulphate solution. Potassium chrome alum melts at 89°, turning green (Tilden, J.C.S. 1884, **45**, 409) ; in solution the change occurs at about 78°. Montemartini and Vernazzi (*l.c.* **8**, 445) state that the saturated solution at 18° contains 28·2% of

$$K_2SO_4 \cdot Cr(SO_4)_3 \cdot 24H_2O,$$

of which 51·75% exists as a violet salt; the saturated solution of the sodium chrome alum contains 94·8% of the salt with $24H_2O$, of which 51·7% exists as a violet salt. Chrome alum is used in paper-making, photography, dyeing, printing, and tanning. Immersion in a bath of chrome alum hardens gelatin films and renders them insoluble, an effect attributed to the fixation of chromic hydrate.

Pure crystallisable violet chrome alum may be prepared by the electrolysis of a solution of potassium dichromate mixed with sulphuric acid. The liquor is circulated in the cathode compartment which is separated from the anode by a porous vessel. The cathode is preferably of carbon. Dilute sulphuric acid is circulated in the anode compartment and the anode may be copper with copper turnings to utilise the SO_4 ions (Chaumat, F.P. 459677, G.P. 265170).

Chrome alum is manufactured from ferrochromium by Chemische Fabrik in Billwarder, vorm. Hell and Sthamer A.G., and Hasenclever, by dissolving the alloy in sulphuric or hydrochloric acid and adding to the solution sufficient alkali to precipitate only the chromium present; the precipitate is converted into chromic sulphate and chrome alum in the usual way (B.P. 187232). In a similar process the same patentees separate about half the iron by crystallisation as ferrous sulphate and centrifuging. The liquor, from 1,000 kg. of ferrochromium and 3,000 kg. of sulphuric acid, is next treated with potassium sulphate, 10 kg. of potassium dichromate, and 3 kg. of sulphuric acid, while sulphur dioxide is passed into the liquor, chrome alum then crystallises (B.P. 187231). The crystallisation of chrome alum is accelerated if the potassium sulphate is added to a solution of chromic sulphate previously acidified with sulphuric acid and heated to 30°–45°, and the solution then cooled rapidly while stirring (I.G. Farbenind. A.G., B.P. 260885). For use as a mordant, a solution of chrome alum is readily prepared by adding sugar or glucose to a hot solution of potassium dichromate and sulphuric acid. Another process depends on the insolubility of a basic chromic sulphate. Aqueous chromic sulphate containing ferrous sulphate produced by dissolving ferrochromium in sulphuric acid is treated while hot with hydrated lime to neutralise the free acid and filtered from $CaSO_4$. The filtrate diluted to 4–5 times its volume with hot water deposits basic chromic sulphate which can be economically converted into $Cr_2(SO_4)_3$ and chrome alum (W. Hene, B.P. 418714).

A violet chrome alum solution requires the normal amount of $NaOH$ for complete precipitation, but after boiling, only $\frac{5}{8}$ of the theoretical amount. Non-ionised SO_4 in the complex varies from half the total SO_4 in a boiled 1% solution to two-thirds the total in a boiled solution of 150 g./l. This latter solution contains the complex $[Cr_4(OH)_2(SO_4)_4 \cdot 12H_2O]$ (Atkin and Chollet, J. Soc. Leather Trades' Chem. 1934, **18**, 356; Ch. Abs. 1934, 6078). Chrome tanning, as affected by the formation of complexes and by the solubility of basic chromic sulphates, is discussed, by the same authors (Cuir tech. 1934, **23**, 142; *cf.* Küntzel, Kinzer, and Stiasny, Collegium, 1934, 213). The p_H of solutions of basic chromic sulphate and the absorption of Cr_2O_3 therefrom during tanning has been studied by Britton (" Hydrogen Ions," 1929). Basic chrome alum solutions are used in the one-bath process of chrome tanning. Following earlier authors, Lumière and Seyewitz (Bull. Soc. chim. 1903, [iii], **29**, 1077) found that Recoura's green basic sulphate, $2Cr_2O_3,5SO_3$, hardens gelatine more efficiently than chrome alum.

Chromium Chlorate, $Cr_2(ClO_3)_6$.—Solutions of this powerful oxidising agent have been prepared in calico printing works by mixing solutions of chrome alum and potassium or barium chlorate. It has been suggested for the production of ungreenable aniline blacks, but is considered to be liable to tender the fibre. The solution has a strong smell of chlorine and gives off oxides of chlorine when heated. It has been proposed as a mordant for catechu browns (*cf.* Knecht and Fothergill, " Textile Printing," 1st ed. 1912, 201; 2nd. ed. 1924, 211, C. Griffin & Co., London).

Chromium Dioxide, CrO_2, and intermediate oxides, $xCr_2O_3yCrO_3$. Manchot and Kraus (Ber. 1906, **39**, 3512) heated blue chromic hydrate, precipitated from chromic chloride solution by ammonia, to 330° in a current of oxygen, and obtained a black hygroscopic powder which on heating to a higher temperature glowed and evolved a volume of oxygen corresponding to $4CrO_2 = 2Cr_2O_3 + O_2$. L. Blanc (Ann. Chim. 1926, [X], **6**, 182) precipitated brown $2Cr_2O_3,CrO_3 = Cr_5O_9$ by adding a solution of a chromic salt to a solution of potassium chromate, but not if the order of mixing is reversed. A table of these intermediate oxides has been compiled by Blanc (*l.c.*, 199).

Chromium Chromate, $CrO_3,Cr_2O_3,7H_2O$.—Jovitschitsch (Helv. Chim. Acta, 1920, **3**, 40) states that when a solution of chromic oxide in HNO_3 is evaporated until excess of acid is removed and the residue dissolved in water and treated with ammonia a brown substance is precipitated which is black when air-dry. Analyses give the formula $Cr_2(OH)_8,H_2O$ or $CrO_3,Cr_2O_3,7H_2O$. It loses $1H_2O$ over H_2SO_4, $2H_2O$ at 105°, and $4H_2O$ at 205°. By dissolving Cr_2O_3 in HNO_3 and evaporating and heating to 290°, a black product is obtained believed to be $CrO_3 \cdot Cr_2O_3$ (*cf.* Jovitschitsch, Monatsh. 1912, **33**, 9; 1913, **34**, 225). For other preparations, *see under* chromic oxide, and the decomposition of CrO_3 by heating.

Chromic Anhydride, Chromic Acid, CrO_3.—This oxide is usually prepared by mixing excess of concentrated sulphuric acid with a saturated solution of potassium or sodium dichromate or by digesting barium chromate with dilute sulphuric acid and evaporating the filtrate. The crystals which separate contain sulphuric acid if made by the first process and either barium dichromate or sulphuric acid if made by the second, and must be purified by crystallisation after addition of the required quantities of either barium chromate or sulphuric acid. Commercial " pure " chromic acid has been known to contain sulphate (Adcock, J. Iron and Steel Inst. 1927, **115**, 369). In one early method Warington (Phil. Mag. 1842, **20**, 453) mixed 10 volumes of cold saturated potassium dichromate solution with 12–15 volumes of conc. sulphuric acid, and collected the separated crystals on a filter of broken glass transferred them to porous plates and recrystallised the crude product from a little water. Bunsen (Annalen, 1868, **148**, 290) mixed 5 parts of sulphuric acid with 11 parts of a solution containing 1 part $K_2Cr_2O_7$, after 24 hours the CrO_3 crystals which separated were filtered off by suction, washed with nitric acid, and heated in a current of dry air at 60°–80°. Zethow (Pogg. Ann. 1871, **143**, 468) states that the nitric acid should be not less than 1·46 sp.gr. An anonymous author (J. Chem. Eng. China, 1936, **3**, 39) treats $K_2Cr_2O_7$ with 68% nitric acid and separates the CrO_3 from KNO_3 by fractional crystallisation. The yield is 90% of CrO_3 of 98% purity, suitable for chromium plating baths (*cf.* Lee and Kung, B, 1937, 901).

Metals Protection Corporation (B.P. 307061) wash the crude CrO_3 with sulphuric acid to remove $NaHSO_4$, or remove the greater part of adhering mother liquor by heating, and precipitate residual sulphuric acid by adding $Ba(OH)_2$, $BaCO_3$, or $BaCrO_4$. Bolley (Annalen, 1845, **56**, 113) had already pointed out that CrO_3 is least soluble in sulphuric acid of the composition $H_2SO_4 + H_2O$. Several methods start from calcium chromate. Kirkhgof, Korzina, and Astrova boil calcium chromate until it is converted into the difficultly soluble $2CaCrO_4.H_2O$, which is filtered off, washed, and decomposed with sulphuric acid, the filtrate from the $CaSO_4$ is treated with sulphuric acid and CrO_3 crystallised and centrifuged (Khim Farm. Prom. 1934, **1**, 38; *cf.* Rakovski, J. Phys. Chem. Russ. 1928, **60**, 13). Vetter, assr. to Natural Products Refining Co. (U.S.P. 2034256), describes the conditions for preparing CrO_3 of high purity by the action of H_2SO_4 on $Na_2Cr_2O_7$. Polyanskii treats a solution of calcium chromate (2 pt.) with H_2SO_4 (1 pt. *d* 1·84) in successive portions, heating on the water bath and removing $CaSO_4$ between each addition, until no more is precipitated; finally CrO_3 is crystallised and purified by Bunsen's method (*v. supra*; Trans. Inst. Pure Chem. Reagents, Sci. Tech. Dept. U.S.S.R. 1929, No. 300, 143). Tanabashi (Japan P. 99439, 1933) treats sodium dichromate with 4–5 times its equivalent of sulphuric acid of 55°–58° Bé, sodium hydrogen sulphate dissolves while CrO_3 is precipitated in fine crystals, which are recrystallised from dilute sulphuric acid and washed with a saturated solution of CrO_3 to remove sulphuric acid. J. W. Boss (U.S.P. 2055961, 2055969) electrolyses a sodium chromate solution, *d* 1·4. This forms a lower layer in a cell of which the upper half is divided by an impermeable partition into an anode and cathode compartment containing respectively as upper layers chromic acid solution and caustic soda solution, each of *d* 1·2. The sodium chromate solution is continuously fed into the lower part of the cell, while $NaOH$ and CrO_3 solutions overflow separately from the upper compartments. Angelini and Panebianco (F.P. 770734) heat chromite mixed with sawdust or peat to 400°, chlorine is then passed over the porous material. It was already known (Moissan, Compt. rend. 1880, **90**, 1357) that chromyl chloride, CrO_2Cl_2, is formed in a similar reaction. With water this gives CrO_3 and hydrochloric acid. Udy (assr. to Electro Metallurg. Co., U.S.P. 1878918) claims an electrolytic process in which an anode of ferrochrome dissolves in sulphuric acid, *d* 1·38–1·52, contained in the anode compartment. CrO_3 is crystallised from the acid.

Chromic anhydride (often termed chromic acid) is a strongly acid substance crystallising in scarlet rhombic bipyramids. Its formula is CrO_3; the acid of the formula H_2CrO_4 has not been isolated. A thermal study of the system CrO_3—H_2O did not reveal the presence of any compound (Buchner and Prins, Z. physikal. Chem. 1913, **81**, 113). The crystals have a specific gravity variously stated, with 2·737/14° and 2·819/20° as limits. The highest value recorded for the melting-point is 198°, (Jaeger and Germs, Z. anorg. Chem. 1921, **119**, 145). When heated to 125° under 16 mm. pressure it sublimes in red needles (Arctowski, *ibid.* 1895, **9**, 29). At a temperature above but near its melting-point it decomposes into chromic oxide and oxygen. Above 250° it is said to yield a residue of the oxide Cr_5O_{12} ($Cr_2O_3{\cdot}3CrO_3$) which may be purified by boiling with water. According to Simon and Schmidt (Z. anorg. Chem. 1924, **152**, 191) this oxide is formed between 370° and 450°. Its existence is supported by the experiments of Honda and Sone (Sci. Rep. Tôhokw, 1914, **3**, 223). A saturated solution of chromic acid at 15° contains 62·4 g. CrO_3 in 100 g. solution. The nature of the ions in dilute solutions of chromic acid has been the subject of many investigations, but the results are in conflict. Britton (J.C.S. 1924, **125**, 1572) from electrometric titration concluded that in dilute solution the ions are H^+ and $HCrO_4^-$. Spitalsky's results are in agreement (Z. anorg. Chem. 1907, **54**, 265). The dissociation to the second stage $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{--}$ is extremely small. Other authors, including Ostwald, have argued that the aqueous solution contains $Cr_2O_7^{--}$ ions.

Chromic anhydride is a powerful oxidising agent. Warm, anhydrous alcohol inflames when dropped upon it, and even dry ammonia gas is oxidised with production of water and nitrogen. Addition of oxalic acid is said to increase its oxidising power. The solution in water, sulphuric acid or acetic acid is largely used as an oxidising agent in organic work. In most of these oxidations precautions must be taken to moderate the velocity of the reaction. When acetic acid is used as the solvent, the substance to be oxidised is usually dissolved in the same solvent, and the oxidising solution slowly added, the temperature being kept sufficiently low, *i.e.* seldom above 100°. Chromic acid, as an oxidising agent, has the advantage that the end of the reaction is frequently indicated by a pure green colour.

It has the property of producing a permanent yellow colour on silk or wool, but not on cotton. The chromium in such material may be converted into lead chromate upon the fibre or further dyed by logwood, etc. Chromic anhydride usually contains sulphuric acid and sulphates or nitrates.

Chromates.—All chromates are prepared directly or indirectly by the action of oxidising agents on ferrochrome or on chromite, FeO,Cr_2O_3 (*q.v.*). Both the normal and acid chromates are of importance industrially. The normal chromates of sodium and potassium, M_2CrO_4, are readily converted into the dichromates, $M_2Cr_2O_7$, by the addition of sulphuric acid to their solutions, which then change from yellow to orange. A basic chromate, orange chrome, $PbO{\cdot}PbCrO_4$, is also manufactured in connection with chrome yellow, $PbCrO_4$.

A great number of processes have been proposed for the conversion of Cr_2O_3 in chromite into CrO_3; the oxidising agent is now atmospheric oxygen acting on an alkaline fusion of the ore.

In former times the ore was mixed with about two-fifths of its weight of potassium nitrate and ignited on the bed of a reverberatory furnace, the oxygen required for the oxidation of sesquioxide into the anhydride and the potassium for its conversion into potassium chromate being both provided by the nitrate. A great saving was introduced by the substitution of atmospheric oxygen as the oxidising agent in place of the nitre, the potassium being supplied by potassium carbonate or, as proposed by Watt, by potassium sulphate (*cf.* Gibbs, assr. to National Electrolytic Co., U.S.P. 901436, 1908).

In the modern process a mixture of chromite, soda ash, and lime is heated in a controlled supply of air to a high temperature in a reverberatory or in a rotating furnace.

Sofianopoulos (J.S.C.I. 1930, **49**, 279T) recommends a furnace charge of a finely powdered (60 mesh) mixture of 340 lb. of chromite (53·6% Cr_2O_3), 270 lb. soda ash (92%), 300 lb. lime (85% alkalinity), and a reaction temperature of 1,400°F. Under these conditions the recovery of soluble sodium chromates was 94·5% of theory, and the method of working described in the original avoids as much as possible the loss due to production of calcium chromate, which in practice was found to be very slowly soluble in boiling water.

In another method of working these difficulties are overcome; fusion of the charge is avoided and the calcium chromate produced is boiled with sodium carbonate in vats fitted with stirrers. The filtrate is concentrated *in vacuo*, and a slight excess of sulphuric acid added, when the greater part of the sodium sulphate separates, the remainder is removed during further concentration, and finally sodium dichromate crystallises out.

The sodium carbonate may be partly recovered if the sodium chromate is converted into dichromate by passing into the solution carbon dioxide under pressure so long as sodium bicarbonate is precipitated. This salt then returns to the process and the conversion of chromate into dichromate is completed by the addition of the required amount of sulphuric acid. The less soluble potassium salt is obtained by adding potassium chloride to the solution of $Na_2Cr_2O_7$. Fusion of chromite with caustic soda has been suggested (G.P. 151135, 163814, and 171089). A direct production of sodium dichromate has been claimed by Bozel-Maletra Soc. industr. de prod. chim. (G.P. 625568), in which the chromite ore is heated in a rotary furnace with soda-ash in a current of air. In a wet process owned by the same Company (J. E. Demant assr.) the chromite is treated with oxygen gas in an aqueous medium under pressure at temperatures above 100° in presence of Na_2SO_4 or other salt yielding active cations (U.S.P. 2012061), or ferrochromium, and $NaOH$, KOH, or K_3PO_4 are the starting materials (U.S.P. 2012062, B.P. 416624). The anodic oxidation of chromic salts to chromates has been studied by Gross and Hickling (J.C.S. 1937, 325), who explain the results by assuming a primary formation of H_2O_2 at the anode. Spent chromic acid baths from oxidation processes are regenerated by electrolytic oxidation in the anode compartment of a divided cell by a method invented by the I.G. Farbenind. A.-G. The same patentees manufacture potassium dichromate by heating a mixture of chromic oxide and potassium hydroxide to 300°–380° in a revolving pan in presence of air or oxygen (B.P. 416744). According to another patent of the same origin, sodium dichromate is manufactured from aqueous sodium chromate containing 475 g./l. of CrO_3 by treatment at 60°–80° with CO_2 under pressure, and cooling without releasing the pressure. The conversion of mono- into dichromate is thus 90%, while $NaHCO_3$ separates and is removed. The filtrate is concentrated to 800–820 g./l. of CrO_3 and again treated with CO_2 to complete the conversion into $Na_2Cr_2O_7$ (I.G. Farbenind. A.-G., B.P. 424821).

The dry method of chromate production has been investigated with the following results:

Calcium and chromic oxides begin to interact in the presence of air to form calcium chromate at 650°; at 700° a 95% yield of chromate is obtained with mixtures containing 2 equivalents of CaO to 1 of chromic oxide and a 60% yield when the ratio is 1 : 1. Pure calcium chromate does not begin to decompose until 1,000° is reached. Sodium carbonate and chromic oxide readily react to form chromate at a temperature below 660°; the salt melts at 800° and remains undecomposed after prolonged heating at 1,000° (M. R. Nayar, H. E. Watson, and J. J. Sudborough, J. Indian Inst. Sci. 1924, **7**, 53).

Alloys.—Various alloys of chromium have been prepared, chiefly by reduction in the electric furnace, by the "thermit" method, or by the usual mixture of molten metals.

Molten *zinc* dissolves but little chromium; a hard and brittle alloy has been obtained in the form of hexagonal lamellæ. *Aluminium* and chromium mixtures, containing between 5 and

55% chromium, separate into two liquid layers, and probably contain a compound, Cr_3Al. The alloys with a low percentage of chromium are brittle, one containing 13% chromium can be powdered in a mortar.

Alloys with *antimony* are brittle, and compounds represented by SbCr and Sb_2Cr are known. Chromium alloys with *copper* with difficulty, but an alloy can be obtained by stirring in copper oxide into a molten alloy of aluminium and chromium (Moissan). The liquid metals are miscible only to a small extent.

Silver and chromium, although partially miscible in the liquid state, form no solid solution. Molten *cadmium* does not dissolve any chromium. Molten mixtures of *lead* and chromium, containing more than 27% lead, separate into this mixture and pure lead.

Platinum-chromium.—V. A. Nemilov (Z. anorg. Chem. 1934, **218,** 33) finds that the Brinell hardness-composition curve of Cr-Pt alloys shows well-marked minima corresponding with compounds Cr_2Pt and CrPt. Examination of the micro-structure confirms the existence of the latter. Alloys quenched from a high temperature show only mixed crystals, from which CrPt separates on annealing. In annealed specimens there is a continuous series of mixed crystals between 0 and 25 atomic %, and another between 65 and 100 atomic % Pt. The electrical resistance rises very steeply with increasing Cr content up to 13 atomic % Cr, beyond which the alloys are no longer ductile. Alloys containing 4–5% Cr have about five times the resistance of Pt, and a higher melting-point. H_2SO_4, HCl, and HNO_3, dilute or conc., show no action either at room temperature or at their boiling-points, on polished surfaces of alloys with a Cr content not greater than 14 atomic %.

Chromium-nickel.—G. Voss (Z. anorg. Chem. 1908, **57,** 34) finds that the system CrNi is homogeneous in the liquid phase with a series of mixed crystals in the solid state, the curve showing a deep minimum at 1,290° and 40–42% nickel.

In the system chromium-nickel, Matsunaga (A, 1930, 680) states the components are miscible in all proportions in the liquid phase; in the solid phase the eutectic m.p. 1,346° contains 49% Ni. The best workable acid-resisting alloy contains 15–35% Cr.

X-ray investigation of the nickel-chromium system by E. R. Jette, V. H. Nordstrom, B. Queneau, and F. Foote (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Pub., 1934, No. 522) shows that below 1,150° there are two terminal solid solutions with an intervening two-phase area. On the Cr side the solubility of Ni in Cr is low, but increases rapidly at over 900°. The solubility of Cr in Ni increases uniformly and rapidly with rise in temperature, that at 1,153° being nearly 53 wt.% Cr, which is beyond the eutectic point as determined by thermal analysis. The only structures observed were body-centred Cr, face-centred Ni, and occasionally rhombohedral Cr_2O_3 (*cf.* Nishigori and Hamasumi Sci. Rep. Tôhoku Univ. 1929, **18,** 491).

Nickel-chromium alloys with less than 90% nickel are non-magnetic.

Cobalt-chromium.—Cobalt and chromium are miscible in all proportions, both in the liquid and the solid states, and yield a mixture of minimum melting-point 1,320° with 47% Cr. Homogeneous alloys, with 30% Cr, when cooled separate into two sets of crystals, Lewkonja, Z. anorg. Chem. 1908, **59,** 325.)

Wever and Haschimoto (Chem. Zentr. 1930, I, 3482), in reconstructing the equilibrium diagram for the system cobalt-chromium, state that on account of the small velocity of diffusion of the components complete equilibrium is attained only with difficulty. Chromium has m.p. 1,765°±10°. Cobalt and chromium are miscible in the fused state in all proportions. The eutectic is at 1,408° and 42% Cr. Up to 38% Cr the mixed crystals are face-centred cubic, whilst above 48% Cr they are body-centred. The compounds Co_2Cr_3 and CoCr (tetragonal, with 8 mols. in the unit cell) probably exist. The temperature of polymorphic α–β transformation is maximal for 7·5% Cr, falling with a higher chromium content. The temperature of magnetic transformation falls almost proportionally to the chromium content. The resistance to corrosion by acid is considerable, being greatest for nitric and least for hydrochloric acid (for the industrially important CrCo alloys, *see* this vol., p. 217*b*, Stellite Alloys).

Copper-chromium.—In the system of copper-chromium there is only partial miscibility in the liquid state with a eutectic near the copper end (1·5% Cr, 1,076°), the limit within which no mixture of the two liquids is formed being 37–93% chromium, above 1,470°. In the solid state only heterogeneous mixtures of two crystal species are obtained, chromium and the eutectic rich in copper. In the ternary system Cr–Ni–Cu the heterogeneity of the Cu–Cr system is 55% removed by addition of Ni (Siedschlag, Z. anorg. Chem. 1923, **131,** 173)

Chromium-molybdenum (Siedschlag, *ibid* **131,** 191—Molybdenum dissolves readily in chromium until the mass contains 25% Mo. The curve showed a eutectic at 1,460°–22·7% Mo. The liquid is homogeneous, but no mixed crystals are formed below 22·7% Mo, the solid consisting of chromium crystals and the eutectic mixture. Above this proportion the solid consists of the eutectic and crystals of molybdenum containing 2·5% chromium.

Carbon-chromium.—These alloys fall into two groups: (1) Those containing 8·5% carbon, completely soluble in hot 24% hydrochloric acid; (2) those containing more than 8·5% carbon, partly soluble in the same acid, obtained by melting chromium (prepared by the aluminium-thermic process) in a crucible of pure carbon at temperature varying from 1,840° to 2,567° for 15 minutes and stirring with a carbon rod. The alloys of the first group leave a residue of practically pure Cr_5C_2, which forms silvery crystals, d. 6·915, m.p. 1,665°. No trace of Cr_4C, described by Moissan, was found. The alloys containing more than 8·5% carbon contain no free chromium, only carbide and graphite. The carbon content of the saturated alloy at 1,840° is 12·42% carbon; at 2,233° 14·03%, and at 2,567° 23·12%. With 24% HCl an alloy dissolves, indicating Cr_4C_2. The insoluble residue contains graphite and Cr_3C_2. This is resistant to all acids and is darker than Cr_5C_2, d. 6·683, m.p. 1,890±10°. It is decomposed by chlorine at a red heat, forming the trichloride and carbon. The chemical composition of the alloys rich in carbon is unaffected by the rate of cooling, but larger crystals are developed when the cooling is retarded. An alloy saturated with carbon boils at 2,570°/8–14 mm. pressure, the vapour being pure chromium (Ruff and Foehr, Z. anorg. Chem. 1918, **104**, 27–46). Maurer and Nienhaus (Stahl u. Eisen, 1928, **48**, 996), from collected analyses, show that the carbides of chromium are Cr_3C_2, Cr_4C_2, Cr_5C_2.

Kraiczek and Sauerwald (Z. anorg. Chem. 1930, **185**, 193) investigated the system chromium-carbon between 0–13·3% carbon by means of heating and cooling curves and examination of micro-structure and density and observed that in the interval between 8·32–9·9% carbon mixed crystals were formed and a transformation occurs at 1,465°. The evidence indicates the existence of Cr_5C_2 and Cr_3C_2, but not Cr_4C or Cr_4C_2. Westgren and Phragmén (*ibid.* **187**, 401) state that the chromium-chromium carbide eutectic has 3·4% carbon, not 4·5%. A eutectic carbide of the formula Cr_7C_3 is indicated in addition to Cr_4C,Cr_3C_2.

Schenck, Kurzen, and Wesselkock (Z. anorg. Chem. 1932, **203**, 159), in studying the synthesis of carbides from the metals and CH_4, find that CH_4 reacts with Cr at 600°–800°, forming Cr_5C_2 and a C-rich mixed-crystal phase containing 11·5% C in equilibrium with the Cr_5C_2 phase. The C content of the mixed-crystal phase can be increased to 12·5% by further treatment with CH_4; this phase probably contains Cr_3C_2.

By means of the equilibrium diagram of the chromium-carbon system, Hatsuta (J. Study Met. 1931, **8**, 81–88) finds four carbide phases, ϵ, η, ζ, and κ, corresponding respectively with Cr_4C (cubic), Cr_7C_3 (trigonal), Cr_3C_2 (orthorhombic), and (?) CrC. A eutectic ($\alpha+\epsilon$) lies at 1,485°, 3·7% C. The ϵ and η phases are peritectically formed thus: $\eta+\text{melt}\rightarrow\epsilon$(1,530°), $\zeta+\text{melt}\rightarrow\eta$ (above 1,600°). The ζ phase probably has the maximum melting-point on the liquidus curve, and forms a eutectic with the κ phase; a transformation takes place at 1,505° in this phase.

Iron-Chromium.—With iron the alloys of chromium are of great interest. The system Cr–Fe on solidification exhibits an unbroken series of mixed crystals. αFe–Cr and δFe–Cr show complete miscibility, while γFe (stable between 906°–1,400°) forms mixed crystals with Cr up to 14% (Bain, Trans. Amer. Soc. Steel Treat. 1926, **9**, 9; Oberhoffer and Esser, Stahl u. Eisen, 1927, **47**, 2021; Maurer and Nienhaus, *ibid.* 1928, **48**, 996; Wever, *ibid.* 1929, **49**, 839; Chem. Zentr. 1931, ii, 2924; Bain and Griffiths, Trans. Amer. Inst. Min. Met. Eng. 1927, **75**, 166). The presence of chromium in iron or steel produces a much finer texture, greater hardness, tenacity, and elasticity, and greater smoothness of fracture. Chromium lowers the Ar_3 point, eventually causing its disappearance, whilst it raises the Ar_2 point of the steel, the proportion of chromium required being less the higher the carbon, *e.g.* with 0·2% carbon, 5% chromium is required. Hence chromium steels are self-hardening (*i.e.* air-hardening). Steels containing 15% chromium have been used for tools and have to be cast to shape. With 0·5% chromium and 0·5% carbon the steel is used for artesian well bits and jars and has no equal in the hardened state. With 1% chromium and high carbon the steel is used in bearing balls, cones, roller bearings, and crushing machinery. These low chromium steels, when well annealed, can be machined. The principal use of chromium is as a constituent of other alloy steels especially nickel steels, to which it imparts greater toughness and hardness. As such it is used extensively in automobile parts and in armour plates which are case-hardened and quenched. Chrome steel is also used in the manufacture of special kinds of files. The alloy is usually prepared of the requisite composition by the addition of a definite amount of "ferrochrome," containing from 40 to 85% chromium, to the molten steel.

Stainless steel cutlery containing Cr 11–14% and C 0·3–0·4% was introduced in 1913. For chemical plant stainless steel may contain Cr 8–18% with Ni 8% or Mn 4%. These alloys resist nitric acid, acetic acid, caustic soda, and ammonia. The steel with 14% Cr and 0·15% C will resist hot but not boiling nitric acid. Wires of a chrome steel containing a high percentage of nickel can be fused into glass like platinum. Laboratory electric furnaces are usually wired with Ni-chrome resistance wire (A. B. Kinzel and W. Crafts, "The Alloys of Iron and Chromium," I, 1937; "Low Chromium Alloys," II (now published), "High Chromium Alloys," McGraw-Hill Book Co. Inc., New York and London, 1937; R. H. Greaves, "Chromium Steels," H.M. Stationery Office, London, 1935). For alloys of chromium, *see* Priestley, Ind. Eng. Chem. 1936, **28**, 1381; for chromium steel in pressure vessel construction, *see* Hopkins, *ibid.* **28**, 1386.

Ferrochrome was formerly prepared from rich chrome iron ores in blast furnaces by the use of coke and hot high-pressure blast, or in crucibles. In 1890 the manufacture was commenced in the electric furnace and has gradually superseded the other methods. In the production of chromium from chromite to form ferrochrome, the iron oxide being reduced, reduction of chromic oxide begins about 1,185°C. Thirty parts of pure carbon are theoretically necessary for every 100 parts of iron and chromium reduced. On the basis of the double carbide Fe_3C,Cr_3C_2 being formed by reduction of the chromite the following reaction occurs:

$$9FeCr_2O_4+50C = [2(Fe_3C,3Cr_3C_2)+3Fe]+36CO$$

The ferrochrome resulting would contain theoretically 10·4% carbon, 31·4% iron, and 58·2% chromium. The ore has to be finely ground and is then mixed with anthracite coal in the proportion of 37 parts of carbon to

100 parts of ore, which forms the above alloy, and charged into the furnace. The power consumption in a 750 kilowatt furnace of the Alby carbide type at Kopperaen, Norway, was 3·0 kw. hours per lb., or 0·68 kw. year per short ton for 5% carbon and 65% chromium ferrochrome. The percentage of carbon in the ferrochrome cannot be kept low by regulating the coal charged into the furnace, but decarburisation can be effected with an oxide slag of iron or chromium after tapping the slag from the first reduction (Trans. Electrochem. Soc. 1913, 176).

S. Eriksson (Jernkont. Ann. 1934, **118**, 530; A, 1935, 1455) confirms the existence of an intermediate α'-phase in the Fe–Cr system (approximate formula $FeCr$) (*cf.* Wever, B. 1932, 469).

The addition of chromium decreases the magnetic properties, but all alloys, to 80% chromium, are magnetic. The magnetic property of chromium is not increased by cooling in solid hydrogen (Compt. rend. 1901, **150**, 687). A carbide of chromium and tungsten of great hardness and of sp.gr. 8·41 has been produced in the electric furnace, and to it the special properties of chrome tungsten steels are probably due. These latter (as well as chrome molybdenum steels), containing up to 3% chromium and 16% tungsten, are used for the manufacture of machine tools. Cobalt is frequently added to both classes of tool steel. Steel containing 12% Cr may be produced by reducing Cr_2O_3 by ferro-silicon above a bath of low-carbon steel (Applied Chem. Rept. 1936, 341).

Basic Oxides.—Two chromium oxides, *chromous oxide*, CrO, and *chromic oxide* or *chromium sesquioxide*, Cr_2O_3, are definite basic oxides, yielding salts with acids in which chromium is present as a divalent or trivalent kation, forming the *chromous* and the *chromic* salts. Chromic oxide can also combine with bases to form salts, the *chromites*, of the type $MCrO_2$, in which the chromium is present in the monovalent anion, CrO_2'. *Chromic anhydride*, CrO_3, is an acid anhydride forming, with bases, salts of the type M_2CrO_4, the *chromates*, or $M_2Cr_2O_7$, the *dichromates*, in which the chromium exists as the divalent anion CrO_4'' or Cr_2O_7''. Other oxides have been prepared and are usually regarded as compounds of the basic and acid oxides, *e.g.* $Cr_2O_3{\cdot}CrO_3$= *chromic chromate* or chromium dioxide CrO_2. These oxides are described on p. 101.

The salts of chromium are coloured shades of violet or green; all solutions of violet chromium salts show similar absorption towards light; the spectrum is due, therefore, to the chromium ion. In solutions of green complex salts the absorption band and limit of complete absorption are both shifted towards the red end of the spectrum.

Chromous Oxide, CrO, is most conveniently prepared by the action of dilute nitric acid on chromium amalgam which dissolves the mercury leaving chromous oxide as a black powder (Dieckmann and Hanf, Z. anorg. Chem. 1914, **86**, 301).

Chromic Oxide, Chromium Sesquioxide, Cr_2O_3.—This compound is produced by the oxidation of metallic chromium and by ignition of chromic hydroxide, chromic anhydride, and certain chromates.

(1) Amorphous: (*a*) Prepared by heating potassium chromate or dichromate with a reducing agent, starch, glycerine, sugar, etc., and washing the residue with hot water. (*b*) By heating ammonium dichromate, according to a number of authors the product is green Cr_2O_3. This reaction has been studied by Harbard and King (J.C.S. 1938, 955). *In vacuo* the product was a black powder containing Cr 61·2% (Cr_2O_3 contains 68·42% Cr); on further heating an olive-coloured substance was obtained (Cr 67·3± 0·5%), this heated in hydrogen at 800° for 21 hours yielded bright green chromic oxide (Cr 68·4%). The thermal decomposition of $(NH_4)_2Cr_2O_7$ appears to yield a non-stoicheiometric compound (*cf.* Ball, J.C.S. 1909, **95**, 87, who by slow decomposition of $(NH_4)_2Cr_2O_7$ obtained a black powder, $3CrO_2{\cdot}H_2O$; Hooton, Proc. Chem. Soc. 1908, **24**, 27, found $H_2Cr_2O_4$; Moles and Gonzalez (Anal. Fís. Quím. 1923, **21**, 204) reported the product as CrO_2. Fischbeck and Spingler (Z. anorg. Chem. 1938, **235**, 185) confirm Hooton's formula. For criticism of these results, *see* Harbard and King, *l.c.*). (*c*) By heating mercurous chromate, preferably without access of air. (*d*) Not in the pure state, by heating chromic hydroxide in air. (*e*) By heating chromic hydroxide in an inert gas, finally to a high temperature, the dark green oxide first produced, glows and turns black and becomes insoluble in acids (Moissan, Compt. rend. 1880, **90**, 1359).

(2) Crystalline.—Preparation: (*a*) By fusion of the amorphous oxide in an electric furnace (Moissan, *ibid.* 1892, **115**, 1035). (*b*) By heating potassium dichromate with sodium chloride (Ditte, *ibid.* 1902, **134**, 336); with tin (Prud'homme, Bull. Soc. Mulhouse, 1889, **59**, 599). It has been observed as a kind of sublimate in pottery furnaces.

Wöhler prepared this oxide in fine, small rhombohedral crystals by passing the vapour of chromyl dichloride through a tube heated to redness. The crystals are isomorphous with corundum and of equal hardness; their sp.gr. is 5·21.

A fine shade of amorphous chromic oxide is produced by heating mercurous chromate, Hg_2CrO_4, in a covered crucible; mercury and oxygen escape, and the oxide remains as a green powder. For the preparation of this substance on the large scale, a great number of methods are recommended; one early method is as follows:—boil a solution of potassium dichromate with half its weight of flowers of sulphur so long as the green hydroxide is precipitated. The addition of a little potash solution, by forming potassium sulphide, accelerates the decomposition. The precipitate is filtered and washed. The sulphur retained in the precipitate may be removed by heating (Lassaigne, Ann. Chim. Phys. 1861, [iii], **14**, 299); *cf.* Siegle & Co., B.P. 461799 and Addn. B.P. 461800; Wöhler (Pogg. Ann. 1827, **10**, 46) heats a mixture of potassium dichromate with its own weight of ammonium chloride and a small quantity of sodium carbonate, and purifies the residue by washing.

According to Barian (Rev. Scient. 1846, **20**, 425), a very pure colour, suitable for colouring fine porcelain, is produced by igniting in a crucible a mixture of 4 parts of potassium chromate and 1 part of starch. The mass is washed free from potassium carbonate and re-ignited.

Chromium green is manufactured together with alkaline-earth and alkali formates by heating a suspension or a solution of an alkaline-earth or alkali chromate at 150°–350° with carbon monoxide under pressure (I.G. Farbenind. A.-G., B.P. 305588).

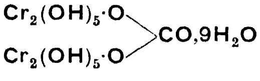
Chromic sesquioxide is a green pigment of great permanence. It is not acted upon by chlorine or sulphur gases or by an intense heat. It melts at 1,990° (Kanolt, J. Washington Acad. Sci. 1913, **3**, 315), at 2,140°±25° (Bunting, Bur. Stand. J. Res. 1930, **5**, 325), and crystallises on cooling a chromium hydroxide (*v.* p. 108).

$$Cr_4(OH)_8O_2,10H_2O$$

or $Cr_4(OH)_{10}O,9H_2O$ (Jovitchitch, Helv. Chim. Acta, 1920, **3**, 46), absorbs carbon dioxide from the atmosphere until a saturation limit is reached. The compound appears to be

$$CO_3[2Cr_2(OH)_6],8H_2O,$$

or



$$\begin{matrix} Cr_2(OH)_5\cdot O \\ Cr_2(OH)_5\cdot O \end{matrix}\Big> CO,9H_2O$$

It can be dried at 100° without losing CO_2, which is, however, liberated by acids (Compt. rend. 1914, **158**, 872).

The oxide is largely used under the names *chrome green* (mixtures of *chrome yellow* and Prussian blue are also called *chrome greens* and must not be confused with the true chrome green) and *ultramarine green* for imparting a green colour to glass, porcelain, etc. It is used for producing the chrome red glaze in ceramic ware, as a pigment in oil and water colours and in printing, and as a mordant in calico-printing and dyeing. Certain hydrated oxides are also used under various names ; their colours are, generally speaking, brighter than that of the anhydrous oxide, but they usually contain small quantities of other substances besides the oxide and water. (For hydrated chromic oxide *v.* R. Fricke and G. F. Hüttig, " Hydroxide and, Oxyhydrate," Academische Verlag Leipzig, 1937).

Guignet's Green; Pannetier's Green; Emerald Green; Verdian, $2Cr_2O_3\cdot 3H_2O$.—This pigment appears to be identical with that formerly manufactured in secret by Pennettier. According to Guignet's method, 3 parts of boric acid and 1 part of potassium dichromate are heated to dull redness in a reverberatory furnace. The mass swells up, evolves oxygen, and becomes of a fine green colour ; it contains the borates of potassium and chromium, or a double borate of those two metals. It is boiled with water, whereby the borate of chromium is decomposed into boric acid and hydrated chromium sesquioxide, potassium borate also remaining in solution. The precipitate is well washed, dried, and finely ground. It usually contains boric acid even after thorough washing, but not if prepared with ammonium dichromate. The washings and mother liquors are evaporated for the recovery of the boric acid.

According to Chem.-Ztg. 1885, **9**, 851, the process then used on the large scale was as follows : The boric acid was first purified by solution in hot water, treating with animal charcoal and recrystallising. The crystals were dried in a centrifugal machine. The mother liquor could be employed three or four times for recrystallisation of fresh portions of acid, but became then too impure for further use. Eight parts of potassium dichromate and 3 parts of purified boric acid were ground into a stiff paste with water, and the mixture in charges of about 1 cwt. heated to dull redness for about 4 hours in a reverberatory furnace. The fused mass was thrown into water, and washed repeatedly by decantation ; the pigment was ground while wet, again washed, filtered, and dried. The first two washings contained considerable quantities of potassium borate, which was recovered by evaporating in leaden pans, adding hydrochloric acid and allowing the boric acid formed to crystallise. The mother liquor was further evaporated and crystallised. The crystals were redissolved, the lead (from the pans) precipitated by hydrogen sulphide, and the filtrate recrystallised. In this manner, from 70 to 75% of the boric acid was recovered.

Guignet's green is the most permanent green pigment known ; it is not acted upon by light or concentrated boiling alkalis ; it is not affected by acids in the cold, but hot hydrochloric acid slowly dissolves it. When heated to 200° it blackens and becomes anhydrous. It is a fine green pigment largely used for the same purpose as the ordinary oxide but is more brilliant, and may replace the dangerous arsenical greens. It possesses good covering power, and can be mixed with other pigments without alteration. When mixed with lead chromate, it is employed for the production of a pale-green colour in landscape painting.

Other *chrome greens* are obtained by the use of sodium phosphate. These always contain some phosphoric acid. They are, however, not as brilliant as the oxide chrome greens. Various methods of preparation are employed. Arnaudon dissolves ammonium phosphate with slight excess of potassium dichromate in a little boiling water, evaporates until the mass solidifies on cooling, heats at 80°, and later at 200°, washes with hot water, dries, and powders. Another method consists in boiling a solution of 10 lb. potassium dichromate with 18 lb. sodium phosphate, adding 10 lb. sodium thiosulphate and a little hydrochloric acid, and boiling until precipitation is complete. The precipitate is washed, ground, and dried.

Blanc and Chaudron (Compt. rend. 1926, **182**, 386) state that the blue form of Cr_2O_3 changes to green at 500° in air, and then resembles Guignet's green (*cf.* B, 1926, 166).

Chromous Salts.—Traube and Goodson (Ber. 1916, **49**, 1679) have prepared chromous salts by the electrolytic reduction of the corresponding chromic salts at a cathode of pure lead. The most favourable conditions for the reduction of violet chromic salts are in moderately acid concentrated solutions with a current density of 2·5 amps. per sq. decimetre. The more common green salts can be used in more concentrated solutions, but require a greater density of current.

Anhydrous chromous salts are white and yield blue solutions which are gradually oxidised in acid solution with the liberation of hydrogen, thus $2CrO+H_2O=Cr_2O_3+H_2$. They are on this account able to reduce organic compounds with double or triple linkings in the presence of water. Acetylene is reduced to ethylene, but not to ethane ; maleic and fumaric acids are readily reduced to succinic acid. Nitrous oxide in the presence of alkali hydroxide is reduced to nitrogen. Nitric acid and hydroxylamine are reduced quantitatively to ammonia (Traube and Passarge, Ber. 1916, **49**, 1692). Chromous salts form stable double compounds with hydrazine which may be precipitated from chromous acetate dissolved in air-free water covered with light petroleum. Chromous dihydrazine chloride, $CrCl_2{\cdot}2N_2H_4$, is a lilac coloured powder sparingly soluble in water.

M. Chatelet (Compt. rend. 1934, **199**, 290) prepared anhydrous $CrCl_2$ by reduction of $CrCl_3$ with H_2 at about 700°. It dissolves in C_5H_5N, yielding a green solution and green crystals of the compound $CrCl_2,2C_5H_5N$. This compound shows traces of oxidation after some hours in the air.; 1 mol. of $CrCl_2$ absorbs 5·48 mols. of dry NH_3 at atmospheric pressure and at room temperature. The higher absorption found by Ephraim and Zapata is attributed to the lower reduction temperature. The composition varies with NH_3 pressure and at zero pressure corresponds with $CrCl_2,3NH_3$, confirming the existence of this compound, but no evidence could be obtained of the existence of $CrCl_2,5NH_3$ by studying the pressure-composition curve. When, however, the $CrCl_2$ is kept saturated with NH_3 at 22° and 76 cm., the colour changes from pale green to violet-rose, and in 20 hours the product corresponds with the composition $CrCl_2,5NH_3$, and its composition does not vary over changes of NH_3 pressure from 11 to 83 cm.

Chromic Hydroxide is precipitated from a solution by caustic alkali or ammonia, but can only be obtained pure by use of the latter reagent owing to adsorption of the fixed alkali by the precipitate. The water retained varies with the method of drying.

A. V. Rakovski and T. Poljanski (Trans. Inst. Pure Chem. Reag. U.S.S.R. 1931, No. 12, 11–16) find that Cr hydroxide free from Cl' may be obtained by reducing $Na_2Cr_2O_7$ with CH_2O in presence of HCl, precipitating with NH_3 and washing with dilute NH_3 and then with H_2O. Preparations made from the sulphate cannot be freed completely from SO_4. Hahn (Ber. 1932, **65**, [B], 64) recommends 15 g. $NaNO_2$, 15 g. NaN_3 in H_2O (250 c.c.) as a reagent for obtaining a pure, dense, easily filtered form.

A colloidal solution of hydrated chromic oxide was prepared by Graham (Phil. Trans. 1861, **151**, 183) by dialysis of a solution of freshly precipitated chromic hydroxide in chromic chloride solution in water. After 30 days' dialysis the deep green solution showed 4·3 parts HCl to 95·7 parts Cr_2O_3, after 38 days 1·5 acid and 98·5 Cr_2O_3.

Hein and Bär (Kolloid-Z. 1931, **57**, 47–49) find that compounds of the type $CrX_2{\cdot}OR,3NH_3$ (where X is a halogen and R an alkyl radical) are precipitated when NH_3 is added to a solution of CrX_2 in the ether R_2O. They dissolve in H_2O with hydrolysis and at sufficient concentration a gel of $Cr(OH)_3$ is formed. The gels are fairly stable and undergo syneresis.

J. Liesiecki (Rocz. Chem. 1930, **10**, 736) finds that stable chromic oxide sols are obtained by adding washed chromic hydroxide prepared by the action of ammonia on chromic nitrate solution to a solution of chromic chloride; such sols do not need to be dialysed.

Chromic Chloride, $CrCl_3$ or Cr_2Cl_6. The anhydrous chloride is obtained by heating a mixture of carbon and chromium sesquioxide in a current of chlorine. It can be conveniently prepared by Bourion's method (Compt. rend. 1909, **148**, 170) by passing the vapour of sulphur chloride, b.p. 138°, over the oxide gradually raised to a red heat. It forms pale-violet scales of sp.gr. 2·782 (Biltz and Birk, Z. anorg. Chem. 1924, **134**, 125); 2·916 (Crespi, Anal. Fís. Quím. 1928, **26**, 152), it is almost insoluble in water, but dissolves readily, being transformed to the green variety (*v. infra*), if only a minute trace of chromous chloride (1 in 20,000) is present.

Chromic chloride may be prepared in solution by dissolving the hydroxide in hydrochloric acid.

The hydrates of chromic chloride include three isomeric hexahydrates : a green salt,

$$[CrCl_2(H_2O)_4]Cl,2H_2O,$$

a violet salt, $[Cr(H_2O)_6]Cl_3$ (Recoura, Compt. rend. 1886, **102**, 548 ; Ann. Chim. 1887, **10**, 34), and a pale green salt of intermediate constitution, $[CrCl(H_2O)_5]Cl_2H_2O$ (Bjerrum, Ber. 1906, **39**, 1599; Z. physikal. Chem. 1907, **59** 376, 596). The green hexahydrate is partly dehydrated *in vacuo* over sulphuric acid and yields the tetrahydrate, a pale green powder, chromic dichlorotetraquochloride,

$$[CrCl_2(H_2O)_4]Cl.$$

The green decahydrate,

$$[CrCl_2(H_2O)_4]Cl,6H_2O,$$

crystallises from a strongly cooled solution (66%) of the green hexahydrate (Werner and Gubser, Ber. 1906, **39**, 1823). The latter salt kept for 4 months at 1 mm. over phosphorus pentoxide is dehydrated to the red hemitrihydrate, $CrCl_3,1\frac{1}{2}H_2O$, but if heated slowly to 155° in a current of HCl the red hemihydrate $CrCl_3,\frac{1}{2}H_2O$ is formed.

The formulæ of Werner and Gubser (*l.c.*) explain the behaviour of the green hexahydrate (*supra*); in a freshly prepared solution at 0°, only one-third of the chlorine reacts with silver nitrate. At ordinary temperature the $AgCl$ precipitate may correspond to all values between $1\frac{1}{2}$ and $3Cl$. The solution of the violet hexahydrate yields $3AgCl$. Hantzsch and Torke (Z. anorg. Chem. 1932, **209**, 60) prepared a bright bluish-green hydrate I from $[Cr(H_2O)_6]Cl_3$ and a dark green hydrate II from $[Cr(H_2O)_4Cl_2]Cl,2H_2O$, by the addition of NH_4OH and NH_4Cl. (I) is readily soluble in acids, (II) less soluble. The formulæ suggested are (I) $Cr(OH)_3,3H_2O$ and

$$\text{(II)}\ [Cr(H_2O)(OH)_3],2H_2O.$$

On passing hydrogen chloride through a concentrated solution of green chromic chloride a heliotrope-coloured double chloride, $CrCl_3,HCl,xH_2O$ (x approx. 6) is precipitated. The substance is insoluble in methyl and ethyl alcohols, and in water gives a pale red solution which immediately turns green (Partington and Tweedy, J.C.S. 1927, 2899).

Chromyl Dichloride, CrO_2Cl_2.—Moissan (Compt. rend. 1884, **98**, 1581) prepared chromyl chloride by treating dry chromic anhydride with hydrogen chloride. It forms at the ordinary temperature but the action is accelerated by heating. It may also be made by distilling potassium bichromate (3 parts) and common salt (3 parts) with sulphuric acid (9 parts) in an atmosphere of carbon dioxide. The corresponding bromide and iodide cannot be made by this method, but the fluoride can, the formula for the latter being CrO_2F_2 (Gazz. chim. ital. 1886, **16**, 218). H. D. Law and F. M. Perkin (J.C.S. 1907, **91**, 191) found that the best way of preparing this compound is to dissolve chromic anhydride (50 g.) in strong hydrochloric acid (170 c.c.) to which is added 100 c.c. of strong sulphuric acid, 20 c.c. at a time. Chromyl chloride sinks as a red liquid and may be separated in a tap funnel. B.p. at 760 mm. is 116·7°, m.p. −96·5° ±0·5°. It is a deep red liquid resembling bromine. Two specimens had $d_4^{-4·7}$, 2·0528–2·0515; d_4^0 1·9591–1·9582; d_4^{25} 1·9124–1·9113 (Moles and Gómez, Z. physikal. Chem. 1912, **80**, 513). Its vapour is not dissociated at 181°C. When heated in a closed tube to 180°–190° trichromyl chloride, $(CrO_2)_3Cl_2$, is formed. This is a black, non-crystalline powder deliquescing in air. Chromyl dichloride reacts with phosphorus trichloride in carbon tetrachloride solution to form $CrOCl,POCl_3$ and PCl_5.

Chromous Bromide, $CrBr_2$.—A white salt giving a blue solution, prepared by Moissan by passing bromine vapour with nitrogen over heated chromium.

Chromic Bromide, $CrBr_3$, is formed like the dibromide, by passing excess of Br over heated Cr. It is a dark green powder and forms two isomeric hexahydrates, green and violet, corresponding to the similarly coloured hexahydrates of $CrCl_3$.

Chromious Iodide.—Hein and Wintner-Hölder (Z. anorg. Chem. 1931, **202**, 81–89) prepared pure CrI_2, m.p. 790°–795°, by heating electrolytic Cr with an excess of I in N_2 or vacuum at 1,150°–1,200°, and removing the excess of I from the product by heating at 200°. Two forms, viz., greyish-white and dark brown, exist. CrI_2 has an appreciable decomp. pressure at 400°–700°, but in presence of a trace of I vapour this is strongly depressed, and increases only very slowly with rise of temperature. Iodine reacts, but not very readily with CrI_2, at 300°, a product containing more than 91% CrI_3 could not be obtained. It reacts vigorously with pyrophoric Cr at 300°, with partial formation (67%) of CrI_3.

Chromic Fluoride, $CrF_3,4H_2O$.—This product, prepared by dissolving chromic hydrate in hydrofluoric acid, is used in the printing and dyeing of woollen goods. (For preparation, *v.* 1937, B, 1199). It is a fine, crystalline, green powder, very soluble in water, but it has a corroding action on glass, and is therefore best kept in lead or wooden vessels. It may be used as a mordant with both vegetable and animal fabrics, and is often employed in the place of acetate or nitrate of chromium for printing, and, in general, gives finer results. Alizarin dyes, cœruleïn, galleïn, etc., and logwood extracts, are fixed as perfectly as with acetate of chromium. One advantage is that it is marketed as a solid. Its effect on wool in after-chroming baths has been criticised (Knecht, Lawson, and Loewenthal, "Dyeing," II, 632, London, 1925). *Chromium silicofluoride*, prepared by dissolving the oxide in hydrofluosilicic acid, has also been used in dyeing and printing in place of the fluoride, and is stated to give better results.

Chromium Nitride.—Valensi (Compt. rend. 1928, **187**, 293) prepared chromium nitride as a brown crystalline powder by heating chromium in pure nitrogen. It gives dissociation isotherms between 810° and 1,200° analogous to those of palladium and hydrogen, which indicate the formation of the compound CrN. The temperature, 1,015°, at which the dissociation pressure is 760 mm. agrees with the calculated value.

Chromium compounds with nitrogen prepared by passing ammonia over chromium heated to 800° show the existence of two phases. The first phase is homogeneous for a considerable range of concentration which probably includes 33 atomic per cent. nitrogen corresponding to the formula Cr_2N. The chromium atoms are arranged in a hexagonal lattice with the densest spherical packing, the nitrogen atoms probably being distributed at random in the spaces of the lattice. The second phase corresponds to the formula CrN with $NaCl$ structure. X-ray examination of a nitrogenous ferrochrome (60·3% Cr, 2·4% N, 0·7% Mn, 2% Si, 0·2% C) showed hexagonal CrN (Blix, Z. physikal. Chem. 1929, B, **3**, 229).

In the system Cr–N the hexagonal β-phase has a "superstructure," the cell volume of which is three times as large as that of the hexagonal close-packed lattice. The upper and lower limits of the region of homogeneity of the β-phase are 11·9% N (Cr_2N) and 9·30% N respectively (S. Eriksson, A, 1935, 1455).

Chromium Azide, $Cr(N_3)_3$ (Mandala and Comella, Gazzetta, 1922, **52**, (i), 112) was prepared by prolonged treatment of an absolute alcoholic solution of crystalline chromium nitrate with sodium sulphate, and evaporation of the filtered liquid with the calculated proportion of sodium azide in a vacuum. It forms a highly hygroscopic dark green amorphous mass.

Chromous Hydrazine Compounds (Traube and Passarge, Ber. 1913, **46** 1505) can be prepared by suspension of chromous acetate in air-free water covered with a layer of light petroleum. The acetate is dissolved by addition of the exactly necessary quantity of dilute acid, and then a solution of hydrazine hydrate or sulphate added. The salt precipitates readily and is washed with water, alcohol, and ether. Chromous dihydrazine chloride, $CrCl_2,2N_2H_4$, and the bromide, $CrBr_2,2N_2H_4$, are lilac-coloured compounds, the iodide, $CrI_2,2N_2H_4$, is greyish-blue.

Chromium Nitrate.—Jovitschitsch (Monatsh. 1912, **33**, 9–18), by dissolving strongly heated chromic oxide in hot concentrated HNO_3 (d. 1·4), obtained a solution from which the hydrate, $Cr_2(NO_3)_6,15H_2O$, crystallises on cooling in the form of dark brown prisms (a.b.c.=1·4210 : 1 : 1·1158, $\beta=93°\ 10'$). In contact with dry air the crystals lose $6H_2O$ with the formation of a grey-coloured hydrate, $Cr_2(NO_3)_6,9H_2O$. Partington and Tweedy by dissolving chromic hydrate obtained the salt $Cr_2(NO_3)_6,25H_2O$ (J.C.S. 1926, 1142).

Chromium Silicides.—Chromium silicides may be prepared by heating the two elements or mixtures of chromic oxide and silicon carbide in the electric furnace; compounds represented by $SiCr_3$, $SiCr_2$, Si_2Cr_3, and Si_2Cr, have been prepared. They are crystalline and very hard—$SiCr_2$ is harder than corundum—and are not attacked by ordinary acids, though attacked readily by hydrofluoric acid and by aqua regia (Lebeau and Figueras, Compt. rend. 1903, **136**, 1329; Matignon and Trannoy, *ibid.* 1905, **141**, 190; Frilley, Rev. métal. 1911, **8**, 476; Baraduc-Muller, *ibid.* 1909, **6**, 157; 1910, **7**, 698).

B. Boren (Arkiv. Kemi, Min. Geol. 1934, **11A**, No. 10, 28 pp.) inferred the formation of the following compounds in the system Cr–Si. Cubic crystals of Cr_3Si with *a* 4·555Å. and 8 atoms in the unit cell, a phase of uncertain composition and structure stable only at about 1,000°; $CrSi$, cubic, *a* 4·620Å., space-group T^4, 8 atoms in the unit cell, structure analogous to that of $FeSi$; $CrSi_2$, hexagonal, *a* 4·422, c 6·351Å., space-group D_6^4.

Chromium Borides.—Moissan prepared hard amorphous CrB from the two elements in the electric furnace (Ann. Chim. Phys. 1896, [vii], **8**, 565). Wedekind and Fetzer employed a mixture of chromic oxide, aluminium powder, and powdered boron, and obtained crystalline CrB (Ber. 1907, **40**, 297). Andrieux prepared Cr_3B_2 by electrolysis of a fused mixture of B_2O_3, Cr_2O_3, MgO, and MgF_2 (Ann. chim. 1929, [x], **12**, 486).

Potassium Chromate, K_2CrO_4, is prepared, as already described, from chrome ore. It may be produced by adding potassium hydroxide to a solution of the dichromate. It crystallises in anhydrous, yellow, rhombic prisms isomorphous with those of potassium sulphate, sp.gr. 2·71 (Kopp). 100 parts of water dissolved of potassium chromate

0°	30°	60°	105·8°
57·11	65·13	74·60	88·8

105·8° being the boiling-point of the saturated solution (Koppel and Blumenthal, Z. anorg. Chem. 1907, **53**, 262). The solution has a fine yellow colour, a distinct yellow tinge is imparted by 1 part in 400,000 parts of water. The solution has an alkaline reaction. Like all chromates the salt is poisonous (*v.* CHROMIUM, *supra*).

When heated, it reddens and fuses without decomposition; heated with reducing agents such as sulphur, it is reduced to chromium sesquioxide. The addition of an acid, even carbonic acid, determines the decomposition into potassium dichromate. It forms double salts with the chromates of the alkaline earths and lead.

Potassium chromate is not largely used, the dichromate, on account of its higher percentage of chromic acid, being generally preferred.

Potassium Dichromate, $K_2Cr_2O_7$, m.p. 389·4°±0·5°.—This important salt, generally known as "bichromate," or "bichrome," is prepared in large quantities by the methods already described. Considerably over 10,000 tons are annually produced in Great Britain.

It crystallises in anhydrous, red, tabular prisms belonging to the triclinic system, of sp.gr. 2·70, and of intensely metallic, bitter taste. At bright redness oxygen is evolved, and the normal chromate and chromic sesquioxide result. Acid chromates, of composition $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$, appear to exist in solution within certain limits of concentration.

100 parts of water dissolve at 0°, 4·64 parts; at 30°, 18·13 parts; at 60°, 45·44 parts; and at 104·8°, 108·2 parts; 104·8° being the boiling-point of the saturated solution (Koppel and Blumenthal, Z. anorg. Chem. 1907, **53**, 263).

The salt separates from the fused state as a compact mass of dark brownish-red tabular crystals with marked reduction in volume. On further cooling the crystals change to a loose, orange-red powder, the transition being 236·8°±0·5°. The unstable monoclinic form changes to stable triclinic crystals at this temperature (Robinson, Stephenson, and Briscoe, J.C.S. 1925, **127**, 547).

Potassium dichromate is used in the preparation of chrome pigments, of "discharge" for Turkey red, etc., for the production of a large variety of colours in calico-printing and dyeing, and in the manufacture of safety matches. In solution with sulphuric acid, it is used as a bleaching agent for tallow, palm oil, etc., in the oxidation of anthracene to alizarin, in the manufacture of aniline violet, and in many other organic oxidations. It is also used in the two-bath process of chrome tanning. The pelt is immersed first in the dichromate solution and then in a solution of sodium thiosulphate acidified with HCl.

When mixed with organic substances it is reduced on exposure to light; gelatine in such circumstances is rendered insoluble. This reaction is taken advantage of in the "carbon" process of photographic printing. The gelatine is mixed with a pigment of any colour, and the paper carrying this film is sensitised by floating on a solution of potassium dichromate. On exposure under a negative, the gelatine in those portions exposed to the light becomes insoluble, and retains the pigment, while the portions protected by the darker parts of the negative are almost unacted upon, and may be dissolved in warm water. In this manner, photographs of any desired colour, and of great permanence, may be produced.

In the *oil-process* gelatine-coated paper may be sensitised with bichromate and exposed under a negative and, after developing the print in water at 25°, it is pigmented with a suitable oil-ink, since the hardened gelatine has the property of fixing greasy inks. In the corresponding gum-bichromate process the paper is coated with a solution of gum arabic and bichromate. For the *carbro* process a bromide print is soaked in water and squeegeed into contact with the sensitive tissue of the carbon process. The silver grains of the print reduce the bichromated gelatine, rendering it insoluble, so that after separation of the tissue it may be developed in hot water. In the *bromoil* process a bromide print is bleached in a bichromate bath, whereby the gelatine of the silver image becomes insoluble, fixed, washed, and the hardened gelatine pigmented by brushing on an oil-ink as in the oil-process.

Sodium Chromates.—The normal chromate $Na_2CrO_4,10H_2O$, and the dichromate

$$Na_2Cr_2O_7,2H_2O,$$

may be prepared by methods similar to those already described under Chromates (*q.v.*), but without the details which now follow. According to Nic. Walberg (Dingl. poly. J. 1886, **259**, 188), 6 parts of powdered chrome ore (44% Cr_2O_3) were mixed with 3 parts of soda ash (92% Na_2CO_3) and 3 parts of chalk, and heated in charges of 1 ton in a reverberatory furnace for 8 hours. The mass is lixiviated to produce a solution of 45°B., boiled down to 52°B., and allowed to crystallise in leaden pans. The crystals are first dried by a centrifugal machine and finally heated to 30° in a drying chamber, where they crumble to a yellow, anhydrous powder containing about 96% of the normal chromate.

For the production of dichromate, these crystals are dissolved to a solution of 40°B. and treated with sufficient chamber acid to determine the conversion into the dichromate, the right point being found by potassium iodide and starch paper. Sufficient neutral sodium chromate is then added to bring the percentage of CrO_3 to about 72·5. The liquor is cooled in lead tanks to 1°, and the sodium sulphate crystallised out. The liquor is drained off, filtered if necessary, and evaporated to dryness in an iron pot, with constant stirring. The residue is powdered while still hot. If the amount of CrO_3 be allowed to exceed 72·5%, the product is damp and cannot be stored in wooden casks. An analysis of this substance showed CrO_3 72·3, Na_2O 26·20, SO_3 1·40.

Modifications in the method of manufacture by Ulm (Chem.-Ztg. 1914, **38**, 670; J.S.C.I. 1914, **33**, 917), consist in the use of caustic alkali in the place of alkali carbonate, and in the employment of only half the sodium carbonate required to decompose the ore, the remainder being replaced by sodium sulphate, formed in the later stages of manufacture.

Normal Sodium Chromate forms large, efflorescent crystals of the composition $Na_2CrO_4,10H_2O$, isomorphous with Glauber's salt. Unlike potassium chromate, it is less soluble than the dichromate; it is, however, more soluble than potassium chromate, the saturated solution at 18° contains 40·10% Na_2CrO_4 (Mylius and Funk, Ber. 1897, **30**, 1718).

Other hydrates with 6 and 4 mols. of H_2O are known. Their transition temperatures have been suggested as convenient fixed points in thermometry (Richards and Kelley, J. Amer. Chem. Soc. 1911, **33**, 847).

Sodium Dichromate, $Na_2Cr_2O_7,2H_2O$, crystallises in thin, six-sided prisms of a fine hyacinth-red colour, and is very soluble in water, 100 parts of water at 30° dissolving 197·6 parts $Na_2Cr_2O_7$ (Schreinemakers, Z. physikal. Chem. 1906, **55**, 91). It is hence more than 10 times as soluble as potassium dichromate (18·12 parts), which it frequently replaces. (For a difference in properties, *see* Robinson *et al.*, *l.c.*)

Ammonium Chromate and Dichromate are prepared by mixing in proper proportions solutions of ammonia and of chromic acid. The dichromate, on heating, yields water and a mixture of equal volumes of nitrogen and nitrous oxide and leaves a residue of chromic oxide mixed with a higher oxide of chromium (Harbord and King, *l.c.*).

Ammonium chromate may be also manufactured by treatment of sodium chromate solution with ammonia and saturating with carbon dioxide, whereby sodium bicarbonate is precipitated.

Calcium Chromate, $CaCrO_4,2H_2O$, is largely produced in the manufacture of chromates from chrome iron ore. The dihydrate exists in monoclinic α and rhombic β forms. The anhydrous salt formed at 200° is less soluble at 100° (0·42 g.) than at 0° (4·31 g. in 100 g. solution) (Mylius, Ber. 1900, **33**, 3689).

Barium Chromate, $BaCrO_4$, is a canary-yellow powder, known as *Yellow Ultramarine* or *Lemon Yellow*. It is produced by the addition of a chromate to a solution of a salt of barium.

Barium chromate is insoluble in water and acetic acid, soluble in hydrochloric and nitric acids. On treatment with a boiling solution of chromic anhydride, it dissolves, and crystallises on cooling as a yellowish-red powder consisting of the dichromate $BaCr_2O_7,2H_2O$.

Both barium and calcium chromates have been employed as pigments, but are now little used on account of their lack of brightness and covering power.

Lead Chromates.—The neutral lead chromate $PbCrO_4$ is best produced by the action of a solution of lead acetate on a solution of a chromate. Thus produced, it is of a fine lemon-yellow colour, insoluble in water and dilute acids. At 25° the solubility of $PbCrO_4$ in water is $5{\cdot}8\times10^{-5}$ g./l. (Ishibashi and Funakoshi, J. Chem. Soc. Japan, 1936, **57**, 1028). When heated at 250° it becomes reddish-brown, at a higher temperature it fuses, and finally evolves oxygen with the formation of chromic sesquioxide and a basic lead chromate. On account of this evolution of oxygen the substance is frequently used for combustions in organic analysis.

Lead chromate is soluble in cold lime water or caustic alkali, but is not dissolved by hot lime water. For this reason, in immersing, calico coloured with chrome yellow in lime water, for the production of an orange colour, care should be taken that the solution is hot.

When heated with the calculated amounts of caustic alkali part of the chromic acid may be removed, with the production of basic lead chromates of colour varying from orange to vermilion.

The *normal chromate* is largely used as a pigment, and for calico-printing, and is the essential constituent of various chrome pigments as *chrome yellow*, *Paris yellow*, and *Leipsic yellow*. The name *Cologne yellow* was originally given to chrome yellow containing a mixture of lead chromate and lead sulphate, but the latter compound is also present in most of the bright yellows known commercially as "genuine" chrome yellows.

Chrome Yellows.—The finest chrome yellow is produced by precipitation; the lead acetate used should not be basic or the product will be of an orange colour; the solution should be dilute, and the lead salt should be in excess; the presence of excess of chromate is liable to "turn" the yellow, *i.e.* to produce an orange tinge. The substances used should be technically pure. According to B.P. 416744, 1933, one method of manufacture from chromic acid consists in adding this acid to a suspension of lead oxide or carbonate in hydrofluoric, fluoboric, or fluosilicic acid, at a rate which is not greater than the velocity of reaction of the latter acids with the lead compound. Pure chrome yellow, $PbCrO_4$, is too expensive for most purposes, is liable to darken in colour, and does not exhibit the required range of tones. A series of "genuine" chrome yellows is manufactured by mixing the precipitating chromate solution with an appropriate quantity of sulphuric acid, Glauber's salt, or alum, the latter salt for *American chrome-yellow*. The lead chromate is thus precipitated together with any required amount of lead sulphate as mixed crystals of $PbCrO_4$ and $PbSO_4$, the colour being paler as the proportion of lead sulphate is increased. A range of "reduced chrome yellows" is made by the admixture of barytes, gypsum, kaolin, or whiting, which are ground with water and the suspension added to the precipitating tank prior to the reaction. As the customer requires chrome yellows, *e.g.* primrose chrome, lemon chrome, and middle chrome, which for reasons of shade or price contain lead sulphate or fillers, these additions are not in general to be regarded as adulterants. Lemon Chrome A and Orange Chrome B may contain from 25 to 90% barytes. The application to these chromes of the Home Office test for toxicity has been studied (Samuels, J. Oil Col. Chem. Assoc. 1938, **21**, 177). The British Standard specification for lead chromes for paints is 282/1927.

Milbauer and Kohn (Z. physikal. Chem. 1916, **91**, 410) show that the reaction

$$PbSO_4 + K_2CrO_4 \rightleftharpoons PbCrO_4 + K_2SO_4$$

proceeds practically completely in the direction of left to right. From determinations of the stability it is established that the solid phase $PbSO_4$ cannot exist in the presence of K_2CrO_4, K_2SO_4 and $PbCrO_4$, and that the existence of double salts is unlikely. The strong adsorption rendered the determination of the mass-action curve difficult. The general results indicate that the manufacture of chrome yellows can be carried out from lead sulphate and that various shades can be obtained by varying conditions, temperature, concentration, and time. It follows also that an excess of lead acetate should be used in the manufacture, since this will secure the absence of K_2CrO_4, which would otherwise rapidly convert the lead sulphate necessary for the particular shade into chromate.

Freshly precipitated $PbCrO_4$ darkens in colour probably because of the change from an unstable rhombic into a stable monoclinic form. When lead sulphate is precipitated simultaneously with lead chromate the two salts form mixed monoclinic crystals which do not darken during settling. The best conditions for precipitation were ascertained by Wagner and Keidel (Farben-Ztg. 1926, **31**, 1567). The monoclinic mixed crystals of $PbCrO_4$ with $PbSO_4$, $BaSO_4$, $CaSO_4$, or $SrSO_4$ are said to be more resistant to light than the rhombic forms and the rhombic mixed crystals first precipitated may be converted into monoclinic by heating their aqueous suspensions (B.P. 403762). Precipitation from dilute solutions with vigorous stirring produces finer particles and brighter shades; while redder tones are obtained in hot solutions. Milbauer and Kohn found that the brightest chrome yellow was obtained by adding a solution of lead nitrate or acetate to a dilute solution of potassium chromate and potassium sulphate (J.S.C.I. 1923, 105A; Chem.-Ztg. 1922, **46**, 1145). They showed that the precipitate consisted of rhombic mixed crystals. These mixed crystals were shown to be solid solutions by X-ray examination (Lederle, Rev. Prod. Chim. 1937, **40**, No. 9, 263). The monoclinic form is said to be superior to the rhombic in resisting light (Wagner, Paint and Varnish Prod. Man. 1934, **10**, No. 5, 10).

The method usually adopted for production of chrome yellow is the following: The two precipitating solutions are prepared separately in wooden tanks and heated by steam pipes. The solutions are either filtered or allowed to settle in the tanks and drawn off from above. They are run together into the precipitating tank, which contains about 200 gallons. The chrome yellow is allowed to deposit and the clear liquid drawn off, more water is added, the whole thoroughly stirred, and the process is repeated three or four times. The pigment is then pumped into a filter press and dried in drying rooms at 30°–50°.

Mixtures of chrome yellows and Prussian blue form the *Brunswick greens*, also known as *chrome greens*, although they are to be distinguished from the more expensive and permanent chromic oxide greens, also termed chrome greens. The Brunswick greens are largely used for ordinary paint work. Monastral Blue has been mixed with chrome yellow for green pigments, and the fastness to light of such mixtures has been discussed by Amies and by Samuels (J. Oil Col. Chem. Assoc. 1938, **21**, 187). By the regulated action of hot alkalis on chrome yellow a series of basic lead chromates is produced ranging in colour from *orange chrome* to *chrome red.*

Orange Chrome.—A washed chrome yellow precipitate consisting of $PbCrO_4$ and $PbSO_4$ is treated at 80°–90° while stirring with the calculated quantity of caustic soda solution until the reaction is completed. The product is washed, filter-pressed, and dried as usual (Zerr and Rübencamp, "Farbenfabrikation," 4th ed., Berlin, 1930) ; or the freshly precipitated lead chromate+lead sulphate is boiled with milk of lime—with the object of producing a basic chromate containing gypsum as a filler. In another process basic lead chloride is first prepared by the action of hot sodium chloride solution on litharge, dichromate solution is then added which forms monochromate with the caustic soda now present and this reacts with the basic lead salt. Orange chromes sometimes contain a colour lake precipitated on the pigment to brighten the shade. Holley ("Analysis of Paint and Varnish Products," p. 214, London and New York, 1912) found 4·87% of organic colour in a pigment containing $PbCrO_4$ 40·56%, PbO 47·24%, $PbSO_4$ 5·49%, which may be compared with a light yellow chrome containing $PbCrO_4$ 68·65%, $PbSO_4$ 31·21%.

Chrome Red is conveniently manufactured by boiling white lead with a solution prepared from dichromate and caustic soda, the washed product which has a dull appearance acquires a brilliant red colour after treatment with dilute sulphuric acid, the pigment is then washed and dried as usual. The pigment is not so generally useful as the other lead chromes, for when finely ground the shade changes from deep red towards orange yellow. It may replace cinnabar in distemper painting, but settles out too readily if made into an oil paint. The synonyms of this pigment include the names *Derby red, Persian red, American vermilion, Victoria red, Chinese red.*

Wagner and Schirmer (Z. anorg. Chem. 1935, **222**, 245) studied the products formed by adding KOH to a lead salt and potassium chromate. With increasing KOH the orange red $PbO{\cdot}PbCrO_4$ changes to a pure red substance of the same composition and crystalline form (tetragonal) but of different particle size. The final product was orange red, not uniform, and appeared to contain yellow PbO.

Holley (*l.c.* 220) found in a light American vermilion, $PbCrO_4$ 50·16%, PbO 41·20%, $PbSO_4$ 6·15%; in a deep American vermilion $PbCrO_4$ 53·60%, PbO 40·88%, $PbSO_4$ 4·97%. It may be noted that $PbO{\cdot}PbCrO_4$ contains PbO 40·85%, $PbCrO_4$ 59·15%. For rust prevention, a priming coat of a basic lead chromate paint (which may have an addition of zinc chromate) has given excellent results on properly prepared structural iron and steel work. Chrome yellow paints darken when exposed to the air of towns and are also liable to be darkened by strong sunlight owing to the reducing action of the oil medium on the chromate (Palmer, J. Oil Col. Chem. Assoc. 1925, **8**, 90). Reddy (Official Digest, 1934, No. 130, 328) has compared the different types of lead chromes and zinc chromes as regards grinding, hiding power, paint media, anti-corrosive action, etc. The importance of the yellow and orange chrome pigments is shown by the output in the U.S.A. which in 1935 amounted to 39 million lb.

Scarlet Chromes is the descriptive name given to a series of pigments consisting of mixed crystals of chromate, sulphate, and molybdate of lead (J. Oil Col. Chem. Assoc. 1938, 174).

The lead chromates all possess good covering power and brightness of colour; they are durable, but blacken under the action of sulphuretted hydrogen. They mix well with other pigments, but should not be used with ultramarine, lithopone or other sulphide pigments.

Bismuth Chromates.—The addition of potassium dichromate to a neutral solution of bismuth nitrate gives a yellow flocculent precipitate, $Bi_2O_3,2CrO_3$, soluble in acids (Löwe). On heating, it becomes partly decomposed and turns greenish. K_2CrO_4 and solution of bismuth nitrate, the precipitate formed consists of $3Bi_2O_3,2CrO_3$ (Löwe, 1856), and is quite insoluble in water. Bismuth chromate is used as a pigment (*cf.* Cox, Z. anorg. Chem. 1906, **50**, 226).

Zinc Chromate, Zinc Yellow, or Buttercup Yellow, $ZnCrO_4$, is a beautiful yellow pigment, produced by the addition of hot neutral solution of zinc sulphate to potassium chromate, or by adding a cream of zinc oxide in water to a boiling solution of potassium dichromate. It is slightly soluble in water and readily so in nearly all acids, in ammonia, and in caustic soda.

Zinc chromate can be obtained in various tints and has a good colour. Though not equal to *chrome yellow* in covering power or body, it has the advantage of not blackening by contact with sulphides. It is used for mixing with Prussian blue to form the *zinc greens,* which are faster to light than the corresponding Brunswick greens. The British Standard specification for zinc chromes for paints is 389/1929.

Samples of commercial zinc yellow analysed by Fox, Ellis, and Hirst (J. Oil Col. Chem. Assoc. 1928, **11**, 195 ; *cf. ibid.* 198) showed an average content of ZnO, 42·5% ; CrO_3, 38·4% ; theory for $ZnCrO_4$, ZnO 44·9%, CrO_3 55·1%. The samples contained alkali, up to 11·1% K_2O, in another sample 7·0% Na_2O ; and combined water up to 8·2%. Zinc chromate purchased from chemical supply firms had a similar composition and in one case contained ammonia equivalent to 10·1% $(NH_4)_2O$. The potassium zinc chrome above mentioned gave 15·1% water-soluble (arbitrary method in B.S.S. 254/1926), and the sodium zinc chrome 42·6%. In the discussion (*l.c.* 200), the change of colour in zinc chromate on keeping as a standard in a sealed bottle was mentioned, and also the loss on washing the pigment which could reach 50 to 60%. Brizzolaria *et al.* (Ind Eng. Chem. 1937, **29**, 656) represent the composition by the formula

$$K_2O,4ZnO,4CrO_3,3H_2O.$$

Britton and Evans (J.S.C.I. 1936, **55**, 337T), reporting on seven years' exposure of protective painting on steel, found zinc chromate priming paint very good, although not quite equal to red lead.

Briggs (J.C.S. 1929, 242) confirmed the existence of normal zinc chromate and prepared the following crystalline chromates:

$$9ZrO_2,5CrO_3,12H_2O,$$
$$3Al_2O_3,2CrO_3,6H_2O,$$
$$2Fe_2O_3,4CrO_3,H_2O,$$
$$3SbO_2,CrO_3.$$

Perchromic Acid.—On adding hydrogen peroxide to an aqueous solution of chromic acid, or to an aqueous solution of a chromate acidified with sulphuric acid, a deep blue coloration is produced, which on shaking the solution with ether passes into that liquid.

The reaction is a delicate test for CrO_3 or H_2O_2. The blue perchromic acid is extremely unstable, evolves oxygen and is gradually transformed into chromic acid. Alcoholic alkalies react with the ethereal solution forming salts of blue perchromic acid, *e.g.* $K_2Cr_2O_{12}$, $2H_2O,Tl_2Cr_2O_{12}$ (Schwarz *et al.*, Ber. 1933, **66**, [B], 310). The pyridine compound, however, is $(C_5H_5N)CrO_5$ (*ibid.* **65**, 871). Red perchromates, $M_6Cr_2O_{16}$, are formed by the interaction of alkaline chromate solutions and hydrogen peroxide below 0°, and the free acid is similarly formed from freshly precipitated chromic hydrate. When acidified the solutions evolve oxygen and blue perchromic acid is formed. Schwarz and Elstner (Ber. 1936, **69**, [B], 575) found the etherate CrO_5,Me_2O to be the product when CrO_3 reacted with concentrated H_2O_2 in Me_2O at low temperatures, this explodes already at −30°. The third series of perchromates, the brown salts, coordination compounds of the oxide CrO_4, include perchromateammine, $CrO_4,3NH_3$, formed when H_2O_2 acts on an ammoniacal solution of ammonium chromate. The blue salts were formerly considered to be $MCrO_5{\cdot}H_2O_2$ (Wiede, 1897–1899), but the analyses of Schwarz appear to establish the formulæ quoted above.

Esters of Chromic Acid have been prepared by Wienhaus (Ber. 1914, **47**, 332) by shaking a tertiary alcohol, dissolved in light petroleum or carbon tetrachloride, with an excess of solid chromium trioxide. The ester remains dissolved or suspended in the solvent, from which it can be obtained by evaporation.

CHROMAMMONIUM COMPOUNDS AND DERIVATIVES.

Salts of chromium readily combine with ammonia or substituted ammonias, to form complex compounds in which the chromium atom may be combined with 6 mols. of ammonia, as, for example, in hexammine chromium chloride $[Cr(NH_3)_6]Cl_3$. The ammonia may be substituted by acid groups, the valency and character of the complex radical being determined by the acid and basic radicals in the molecule.

R. Duval has contributed a valuable study of the complex compounds of chromium to Pascal's "Traité de Chimie Minérale," vol. x, pp. 1005–1094, with bibliography, pp. 1094–1098, Paris, 1933. Duval considered that the 2,000 complex chromium compounds then known are classified in his contribution. Prominent authors in the bibliography are Werner, Pfeiffer, Weinland, and Jörgensen and the following general treatises have been published:

Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie."

Urbain and Sénéchal, "Introduction à la chimie des complexes."

Weinland, "Einführung in die Chemie der Komplex-Verbindungen," F. Enke, Stuttgart, 1924.

Pfeiffer, "Organische Molekül-Verbindungen."

Hexammine Chromium Salts (luteo salts), *e.g.* the nitrate, $[Cr(NH_3)_6](NO_3)_3$, are prepared by treating the corresponding purpureo salts with ammonia in cold, concentrated solution (Jörgensen, J. pr. Chem. 1882, (2), **23**, 229; Mills, Phil. Mag. (4), **35**, 245).

Pentammine Chromium Salts (purpureo salts).—Jörgensen (J. pr. Chem. 1879, [2], **20**, 105) prepared the chloride $[CrCl(NH_3)_5]Cl_2$ by reducing violet chromic chloride in a stream of pure, dry hydrogen at a red heat, and adding to the chromous chloride a solution of NH_4Cl in strong ammonia. Air was passed through, HCl added, and the mixture boiled, when a carmine-coloured powder precipitated. It crystallised in octahedra, sp.gr. 1·687, dissolved in 154 parts of water at 16°, and its analysis corresponded to the formula $Cl_2Cr_2(NH_3)_{10}Cl_4$. Jörgensen found that only 4 atoms of chlorine are precipitated by silver nitrate, which confirms Werner's formula given above.

Triammine Chromium Salts.—These compounds have been investigated by Werner (Ber. 1910, **43**, 2286), who employed triammine chromium tetroxide in their preparation. To a well-cooled solution of 30 g. of chromic acid in 300 c.c. of water are added 300 c.c. of pyridine. After remaining half an hour in a freezing mixture, 750 c.c. 3% H_2O_2 are added. The precipitated pyridine perchromate is collected, washed, and added to 90 c.c. of well-cooled 25% ammonia. The precipitated triammine chromium tetroxide $CrO_4,3NH_3$ is collected after 10 minutes and washed with water, alcohol, and ether.

Trichlorotriammine Chromium,

$$Cr(NH_3)_3Cl_3,$$

results when triammine chromium tetroxide is added to cold, concentrated hydrochloric acid. A bluish-grey precipitate is formed, and the filtrate from this deposits the compound after standing 2 days, in dark blue crystals with a greenish tinge. Triaquotriammine-chromium chloride, $[Cr(OH_2)_3(NH_3)_3]Cl_3$, is obtained by treating 1 g. of the dichloroaquotriammine chromium chloride (contained in the grey precipitate above mentioned) with 8 c.c. of water covered with 5 c.c. of pyridine. The resulting solution is filtered, and the hydroxoiodide precipitated by the addition of solid potassium iodide. The chloride is obtained from this by triturating with hydrochloric acid. It forms brownish-red hygroscopic crystals. The corresponding bromine compounds have been prepared.

Chromi-aquo-triammines have been prepared:
$[Cr(NH_3)_3Cl_2H_2O]Cl$,—blue,
$[Cr(NH_3)_3Cl(H_2O)_2]Cl_2$,—reddish-violet,
$[Cr(NH_3)_3(H_2O)_3]Cl_3$,—red.

In solution the mono- compound passes into the di- and the di- into the tri-aquotriammino chromitrichloride (Frowein, Z. anorg. Chem. 1920, **110**, 107–224).

Schlesinger and Worner (J. Amer. Chem. Soc. 1929, **51**, 3520) state that chloropentammine-chromic chloride is converted into insoluble chromium trichlorotriammine, $Cr(NH_3)_3Cl_3$, by heating at 270° in hydrogen chloride until the salt turns from pale red to green. This substance reacts slowly with liquid ammonia to yield the original pentammine; it is possibly a polynuclear compound and its properties are quite different from those of the substance of the same composition described by Werner (J.C.S. 1910, **98**, [ii], 960). If it is heated at 175° in hydrogen chloride, hygroscopic crystalline ammonium chromic hexachloride,

$$(NH_4)_3[CrCl_6],$$

is produced; this substance reacts rapidly with gaseous ammonia with production of the original pentammine. If the triammino salt is heated at 270° in hydrogen chloride a salt having the composition $2CrCl_3,3NH_4Cl$ is formed, and is further slowly decomposed to anhydrous chromic chloride.

Reinecke's Salt, $[Cr(NH_3)_2(SCN)_4]NH_4$, tetrathiocyanatodiamminochromiammonium (Annalen, 1863, **126**, 113; Z. anorg. Chem. 1893, **1**, 135). To three parts of NH_4SCN in incipient fusion, one part of $(NH_4)_2Cr_2O_7$ is added in small portions. The red mass is washed thoroughly with cold water and recrystallised from water or alcohol. Its solution gives precipitates with the heavy metals and organic bases, alkaloids yielding characteristic crystalline compounds—*reineckates* (Rosenthaler, Arch. Pharm. 1927, **265**, 319. For a modern preparation *v.* Dakin, Org. Syntheses, 1935, **15**, 74).

Chromic Oxalates.—There is an extensive literature of these compounds, their double salts and isomerides (Beilstein, 4th ed. II, 522, 523, Erg. II, 226, 227). Special interest attaches to the blue potassium trioxalatochromiate or Gregory's salt, $K_3[Cr(C_2O_4)_3],3H_2O$, which A. Werner resolved into *d*- and *l*- forms by crystallising the strychine salt (Ber. 1912, **45**, 3061). The active isomers possess very high specific rotation and rotation dispersion. Jaeger (Rec. trav. chim. 1919, **38**, 171, "Optical Activity," New York, 1930) found for the *l*-salt, [α] for λ 4740, −486°; λ 5,700, 0°; λ 5800,+515°. Potassium dioxalatodiaquochromiate or Croft's red salt, *trans*- $K[Cr(C_2O_4)_2(H_2O)_2]$, $3H_2O$ is obtained from hot very concentrated solutions of $K_2Cr_2O_7$ and $C_2H_2O_4$. The *cis* isomeride is prepared by moistening a mixture of the powdered substances. With aqueous NH_3 the *cis*- salts become green, whilst *trans*- salts turn brown (A. Werner *et al.*, Annalen, 1914, **406**, 261).

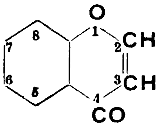
For Detection and Estimation of Chromium, *see* CHEMICAL ANALYSIS.

G. S. B. and J. N. G.

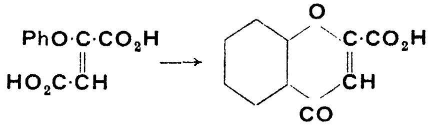
CHROMOFORM is an orange-red crystalline powder formed by the union of methyl dichromate and hexamethylenetetramine. Slightly soluble in alcohol and cold water; readily soluble in hot water. The aqueous solution on boiling, or by treatment with acids or alkalis, evolves formaldehyde.

CHROMOGEN AND CHROMOPHORE *v.* COLOUR AND CHEMICAL CONSTITUTION.

CHROMONE, or benzo-γ-pyrone:



is obtained by the action of sulphuric acid on phenoxyfumaric acid (I), whereby benzo-γ-pyrone-2-carboxylic acid (II) is produced. This, when heated *in vacuo*, yields benzo-γ-pyrone (Ruhemann and Stapleton, J.C.S. 1900, **77**, 1179; Gomberg and Cone, Annalen, 1910, **376**, 228).



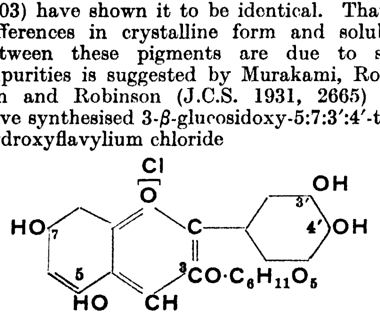
I. II.

Chromone crystallises in colourless needles, m.p. 59°, and its yellow solution in cold sulphuric acid possesses a blue fluorescence.

CHROMOTROPE or **CHROMOTROPIC ACID.** 1:8-Dihydroxynaphthalene-3:6-disulphonic acid.

CHRYSANILINE *v.* ACRIDINE DYESTUFFS.

CHRYSANTHEMIN. A monoglucoside of *cyanidin* (*q.v.*) isolated from the deep red flowers of *Chrysanthemum indicum* Linn. by Willstätter and Bolton (Annalen, 1916, **412**, 136). The chloride $C_{21}H_{21}O_{11}Cl{\cdot}1\frac{1}{2}H_2O$ separated in red-violet leaflets. Hydrolysis of chrysanthemin yielded cyanidin (1 mol.) and glucose (1 mol.). The picrate, difficultly soluble in water, sintered at 165° (decomp.). In its colour reactions—blue-violet with sodium carbonate, pure blue with caustic soda, violet-red with sodium acetate, and purple with ferric chloride—and its high monoglycosidic distribution between amyl alcohol and aqueous acid, it closely resembles *asterin* (Willstätter and Bolton, Annalen, 1916, **412**, 1149) from the purple-red aster, with which Robinson and Willstätter (Ber. 1928, **61**, 2503) have shown it to be identical. That the differences in crystalline form and solubility between these pigments are due to slight impurities is suggested by Murakami, Robertson and Robinson (J.C.S. 1931, 2665) who have synthesised 3-β-glucosidoxy-5:7:3′:4′-tetrahydroxyflavylium chloride



and shown that it is identical with the chloride of chrysanthemin and of asterin and with the product of partial hydrolysis of the cyanidin 3-diglucoside, mekocyanin (Willstätter and Weil, Annalen, 1916, **412**, 231). Chrysanthemin chloride is the second of the remarkable series of anthocyan glucosides which have now been synthesised by Robinson and his collaborators (*see* CALLISTEPHIN).

Chrysanththemin closely resembles the corresponding cyanidin 3-galactoside, *idaein*, from cranberries both in colour reactions and absorption curves, but differs from it in distribution number (Grove and Robinson, J.C.S. 1931, 2723).

Pigments identical with chrysanthemin have been isolated from mulberry fruit by Yamamoto (J. Agric. Chem. Soc. Japan, 1934, **10**, 1046), from the seed-coat of *Glycine Soja* Benth. ("Kuromame") by Chika Kuroda and Mizu Wada (Proc. Imp. Acad. Tokyo, 1935, **11**, 189) and from purple-husked maize by Sando, Milner and Sherman (J. Biol. Chem. 1935, **109**, 203). In the last case its occurrence together with a 3-glucoside of the closely related flavonol quercetin is quoted in support of the theory of flavonols as the precursors of the anthocyanins. It must be noted, however, that cyanidin and quercetin glycosides are the most commonly occurring types of anthocyanin and anthoxanthin found in nature, so that their occurrence together need not be significant.

R. and G. M. Robinson have identified anthocyanins isomeric or identical with chrysanthemin in a great number of other flowers and fruit by means of their qualitative tests (Biochem. J. 1931, **25**, 1687; 1932, **26**, 1647; 1934, **28**, 1712).

Genetical investigations with the Chinese aster by Wit (Dissertation, Gröningen, 1936) show that while pigmentation by cyanidin monoglucoside is sometimes recessive to that by the corresponding 3:5-diglucoside of cyanidin, the cyanidin type of pigmentation is dominant to the pelargonidin type and recessive to the delphinidin type, the production of the differently oxidised anthocyanins probably depending upon the action of multiple allelomorphic genes (*see* ANTHOCYANS).

R. S.-M.

CHRYSAROBIN (B.P., U.S.P.) is a yellow crystalline mixture of substances obtained from *Araroba* or *Goa powder.* The latter varies in colour from primrose-yellow to bronze and purple, and collects, possibly as the result of oxidation of the resin, in the cavities of the stems and branches of *Andira Araroba* Aguiar (Fam. Leguminosæ), a tree inhabiting the forests of Bahia (Aguiar, Pharm. J. 1880 [iii], **10**, 42; *cf.* Greenish, *ibid.* 814). The drug was formerly exported by the Portuguese from Goa, but its origin for a long time remained secret. Goa powder is usually mixed with woody fragments from which it is freed by sifting; it is sometimes termed crude chrysarobin. By extraction of Goa powder with organic solvents (benzene, chloroform) there is left behind on evaporation a yellow crystalline powder, introduced in 1875 by a Bombay firm under the name *Chrysarobin,* which has since been included under this name in the British and United States Pharmacopœias, and is used in skin affections.

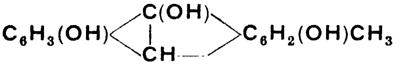
Chrysarobin was originally thought to be a pure, or nearly pure, substance; in reality it is a complex mixture, consisting chiefly of reduced di- and tri-hydroxymethylanthraquinones, which crystallise together and are difficult to separate by purely physical means (*cf.* Hesse, Annalen, 1899, **309**, 53). Later the name chrysarobin was applied to one of the pure constituents, but it is better to reserve this name for the commercial mixture. Tutin and Clewer (J.C.S. 1912, **101**, 290) found the following percentage composition for three samples of commercial chrysarobin :

1. Chrysophanic acid (= chrysophanol)[1] . 2. Emodin monomethylether[1]	6·3	7·2	8·9
3. Emodin	trace	nil	nil
4. Crude anthranol of chrysophanic acid . . .	26	46	62
5. Anthranol of emodin monomethyl ether . . .	small amounts		
6. Monomethyl ether of dehydroemodinanthranol	41·1	13·4	17·7
7. Ararobinol	4·2	4·1	nil
8. Inseparable mixture of partly amorphous substances	23	30	12

[1] About 3 or 4 parts of the former to 1 of the latter.

Of these No. 1 is a methyldihydroxyanthraquinone, No. 3 is a methyltrihydroxyanthraquinone. Nos. 4 and 5 result from Nos. 1 and 2 respectively, by reduction ; they are derivatives of anthranol (9-hydroxyanthracene). No. 6 is a less strongly reduced anthraquinone. No. 7, of unknown constitution, is also an anthraquinone derivative, related to No. 1.

Chrysophanic acid anthranol, $C_{15}H_{12}O_3$, has the constitution

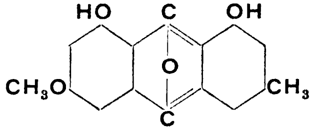


$$C_6H_3(OH)\left\langle\begin{array}{c} C(OH) \\ | \\ CH \end{array}\right\rangle C_6H_2(OH)CH_3$$

and was called chrysarobin by Jowett and Potter (J.C.S. 1902, **81**, 1578). It is obtained from commercial chrysarobin by extraction with light petroleum; by shaking its chloroform solution with sodium carbonate traces of emodin are removed, and after evaporation of the chloroform the residue is crystallised from much ethyl acetate, when it forms lemon-yellow scales, m.p. 202° (corr.) (regenerated from its acetyl derivative the substance melts at 204°). It is insoluble in sodium carbonate, soluble in caustic alkalis to a yellow solution, which becomes red by passing air through it, whereby it is oxidised to chrysophanic acid. The change is complete in 2 hours, as shown by measurement of the oxygen absorbed (Tutin and Clewer, *l.c.*). The reverse change is brought about by hydriodic acid at 130°–140°. Chrysophanic acid anthranol dissolves in sulphuric acid with a yellow colour; it forms a diacetyl compound $C_{15}H_{10}O_3Ac_2$, m.p. 193°, and a triacetyl compound $C_{15}H_9O_3Ac_3$, m.p. 238°.

The *anthranol* of *emodin monomethyl ether* was not isolated by Tutin and Clewer as such, but its presence was inferred from aerial oxidation experiments, which converted it into emodin monomethyl ether.

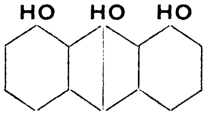
The *monomethyl ether* of *dehydroemodin-anthranol*, $C_{16}H_{12}O_4$, is characteristic of chrysarobin. According to Eder (*v. infra*), its constitution is most probably:



Tutin and Clewer converted it by boiling hydriodic acid into emodin anthranol, a substance containing a methyl group less and 2 hydrogen atoms more; by oxidation with chromic acid they converted it into emodin methyl ether.

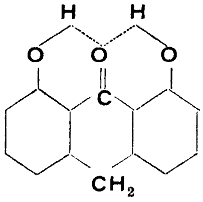
Of the substances 1–6 chrysophanic acid had also been found by Attfield, its anthranol by Jowett and Potter, and emodin monomethylether by Oesterle and Johann (Arch. Pharm. 1910, **248**, 476), but this was the full extent of the agreement among the various investigators of chrysarobin until Eder (Arch. Pharm. 1915, **253**, 1; 1916, **254**, 1) confirmed all the principal results of Tutin and Clewer. He oxidised the commercial substance with air in alkaline solution, and considers that hydrogen peroxide is formed in this reaction, and is responsible for further changes. He thus obtained the following percentages: emodin 0·2, emodin methylether 9·3, chrysophanic acid 22·7, dehydro-emodin anthranol monomethyl ether 18 (=chrysarobol of Hesse?), amorphous products 26. It should be remembered that most of the chrysophanic acid and some of the emodin methyl ether were originally present as anthranols. In his second paper, Eder acetylated and benzoylated chrysarobin and obtained by subsequent hydrolysis up to 14% of chrysophanic acid anthranol, up to 9% of emodin anthranol monomethyl ether, and up to 4% of emodin monomethyl ether, but no chrysophanic acid. The chief discrepancy is that Eder did not find the last of Tutin and Clewer's substances, *ararobinol.* This, according to the latter authors, has the composition $C_{23}H_{16}O_5$, and forms yellow crystals, decomposing without melting at about 225°. It dissolves in alkali with a yellow colour, but, like the methyl ether of dehydro-emodin anthranol, and unlike chrysophanic acid anthranol, it is not readily oxidised by air. It gives a delicate and characteristic reaction with sulphuric acid; a mere trace forms an orange solution, which on gentle agitation gives intense blue streaks; the solution then becomes green, and finally dull grey. Ararobinol gives a triacetyl derivative (decomp. at 225°), is reduced by hydriodic acid to dehydroararobinol, and oxidised, but not quantitatively, by chromic acid to chrysophanic acid.

Chrysarobin is occasonally employed internally as a purgative. Probably its chief constituent, chrysophanic acid anthranol, does not exert a purgative action until it has been oxidised in the alimentary canal (to chrysophanic acid), as is the case with aloïn (Meyer and Gottlieb, "Experimentelle Pharmakologie," Berlin and Vienna, 1933, p. 240). The chief use of chrysarobin is, however, as an ointment in skin diseases (psoriasis), and the active constituent appears to be the anthranol of chrysophanic acid. According to Unna's experiments (Baudisch, Ber. 1916, **49**, 179), the only active synthetic substitutes are the anthranols of 1-hydroxy- and of 1:8-dihydroxy-anthraquinone. The latter, *cignolin,*



is more active in psoriasis than the anthranol of chrysophanic acid (chrysarobin), because it has not the dystherapeutic methyl group.

Baudisch explains the effect of the 1:8-hydroxyls in accordance with Pfeiffer's views by the formula:



"*Dermol*" is prepared by precipitating a bismuth nitrate solution by a solution of chrysophanic acid in sodium hydroxide. "*Anthrarobin*" is the anthranol of alizarin.

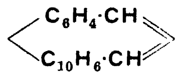
The different methods of extraction cause considerable variation in the composition of commercial chrysarobin and in its physiological action (Pharm. J. 1911, [iv], **87**, 630). Hence Tutin and Clewer consider it fallacious to ask for compliance with exact requirements. (The United States Pharmacopœia states that 1 g. of chrysarobin dissolves in 385 c.c. of alcohol, 13 c.c. of chloroform, 160 c.c. of ether, 30 c.c. of benzene, and 180 c.c. of carbon bisulphide at 25°.) Pure chrysarobin dissolves in concentrated sulphuric acid with a yellow colour, and is insoluble in dilute sodium hydroxide; concentrated sodium hydroxide dissolves it with a green colour. Chrysophanic acid, on the other hand, yields a red solution with concentrated sulphuric acid and dilute sodium hydroxide (Liebermann and Seidler, Ber. 1878, **11**, 1603). Another method to distinguish chrysarobin from chrysophanic acid is to mix 0·05 g. with 0·2–0·3 g. sodium peroxide in a porcelain capsule, add 5 c.c. of alcohol, and after 5 minutes 15 c.c. of water. Chrysarobin yields a wine-lees colour, not destroyed by dilution with water, changing to yellow on the addition of acetic acid; chrysophanic acid yields a cherry-red colour, becoming brighter on dilution (Piñerúa-Alvarez, Ann. Chim. Analyt. 1907, **12**, 9).

G. B.

CHRYSATROPIC ACID. Methoxy derivative of æsculetin (6:7-dihydroxycoumarin).

CHRYSAZIN *v.* ALIZARIN AND ALLIED DYESTUFFS.

CHRYSENE, $C_{18}H_{12}$, or



$$\left<\begin{matrix}C_6H_4\cdot CH\\C_{10}H_6\cdot CH\end{matrix}\right>$$

The highest boiling fractions of coal tar are the richest source of chrysene (for typical treatments of pitch, *see* C. Zerbe and F. Eckert, Brennstoff-Chem. 1934, **15**, 28; J. W. Cook and C. L. Hewett, J.C.S. 1933, 395), although it occurs in tars from many natural products. It is formed by simple distillation of some natural fats, oils and resins, and by drastic dehydrogenation of many natural compounds possessing a related ring-structure, *e.g.* cholic acid (L. Ruzicka and co-workers, Helv. Chim. Acta, 1934, **17**, 200), toad poisons (H. Wieland and G. Hesse, Annalen, 1935, **517**, 22), follicular hormone (A. Butenandi and H. Thompson, Ber. 1934, **67**, [B] 140), Chrysene arises also as a result of pyrolytic treatment of many simpler compounds, *e.g.* phenol (A. Hagemann, Z. angew. Chem. 1929, **42**, 355), tetralin (N. A. Orlow and N. D. Lichatschew, Ber. 1930, **63**, [B], 2179), natural gas (S. F. Birch and E. N. Hague, Ind. Eng. Chem. 1934, **26**, 1008). The action of caustic potash at 300°–310° on indene yields a little chrysene (R. Weissgerber and C. Seidler, Ber. 1927, **60**, [B], 2088), and conisiderable yields are obtained from the same starting material by catalytic dehydrogenation over oxide and sulphide catalysts (B.P. 409837), a similar expansion of an unsubstituted five-membered ring having been observed in the dehydrogenation of perhydrofluorene to chrysene over platinum catalyst (N. Orlow and M. Belopolsky, Ber. 1929, **62**, [B], 1226).

The need for synthetic approaches to condensed cyclic systems of the steroloid type has resulted in the elaboration of several syntheses of chrysene and near derivatives. Thus *cyclo*hexanone and β-(1-naphthyl) ethyl magnesium bromide yield a tertiary alcohol which is cyclised to a hydrochrysene and then dehydrogenated with selenium (J. W. Cook and C. L. Hewett, J.C.S. 1933, 1098; 1934, 365). Variations using Δ'-*cyclo*hexenyl magnesium bromide (J. W. Cook and A. Dansi, J.C.S. 1935, 500) or β-phenyl ethyl magnesium bromide (L. Ruzicka and H. Hösli, Helv. Chim. Acta, 1934, **17**, 470) with α-tetralone have also been effected. Again, an amorphous tetrahydrochrysene has been synthesised by cyclising β-(2-phenanthryl) propionic acid and reducing the resulting keto-tetrahydrochrysene by the Aemmensen method (R. D. Haworth and C. R. Mavin, J.C.S. 1933, 1012). A third recent synthesis of the chrysene ring system due to J. von Braun and G. Irmisch (Ber. 1931, **64**, 2461) and extended by R. Robinson and G. Ramage (Nature, 1933, **131**, 205; J.C.S. 1933, 607) consists essentially in a double cyclisation of $\beta\beta$-diphenyl adipic acid or its chloride to a mixture of isomeric diketohexahydrochrysenes.

Removal of other hydrocarbons from the chrysene fraction of coal tar with carbon disulphide followed by further purification by usual means yields chrysene which is persistently contaminated with a yellow impurity resisting separation by crystallisation, but which may be removed by oxidising agents, *e.g.* perchloric acid (K. A. Hoffmann, Ber. 1910, **43**, 1086), nitric acid and alcohol (Liebermann, Annalen, 1871, **158**, 299; *see also* Schmidt, J. pr. Chem. 1874, [ii], **9**, 250, 270). Other methods recommended for the purification of chrysene are separation through the characteristic 2:7-dinitroanthraquinone complex (Schmidt, *l.c.*) and combination of the impurity with maleic anhydride (E. Clar and L. Lombardi, Ber. 1932, **65**, [B], 1411). For small quantities the method of chromatographic adsorption (*v.* CHEMICAL ANALYSIS, Vol. II, p. 628) is suitable, A. Winterstein and co-workers having identified the impurity (*see also* CHRYSOGEN) as naphthacene (Naturwiss. 1934, **22**, 237; Z. physiol. Chem. 1934, **230**, 146, 158).

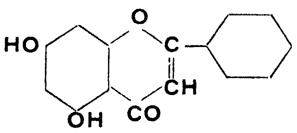
Pure chrysene forms colourless rhombic plates m.p. 250°, b.p. 448°, which exhibit in the solid state or in solution a red-violet fluorescence. It is best characterised by the 2:7-dinitroanthraquinone complex (Schmidt, *l.c.*; Haworth and Mavin, *l.c.*). For a colour reaction of chrysene, *see* Ditz (Chem.-Ztg. 1907, **31**, 445).

Substitution products of chrysene are obtainable by classical methods but are of little immediate importance. K. Funke and J. Ristic have recently determined the orientation of a number of chrysene derivatives by conversion to known carboxylic acids (J. pr. Chem. 1936, [ii], **146**, 151). The direct introduction of a carboxyl group by treatment with oxalyl chloride at 160°–170° is noteworthy (Liebermann and Zsuffa, Ber. 1911, **44**, 207; Weitzenböck and Lieb, Monatsh. 1912, **33**, 551) as is also chrysoquinone, an *o*-quinone obtainable by chromic acid oxidation of the hydrocarbon. Hydrogenation products are also of interest, but complete agreement on the constitution of products of catalytic hydrogenation of chrysene has not yet been reached (J. von Braun and G. Irmisch, Ber. 1932, **65**, 883; A. Spilker, Angew. Chem. 1935, **48**, 368). A mixture of naphthalene and its hydrides results from pyrolytic decomposition of chrysene in presence of hydrogen over ferric chloride at 440° (N. Orlow and N. Lichatschew, Ber. 1929, **62**, [B], 719, 1378).

Chrysene has not yet found extensive industrial use, although patents have been secured for its use in the manufacture of dyestuffs. Thus 1:4-quinones are condensed with an aminochrysene or a derivative of the same in high-boiling solvents and in presence of mild oxidising agents to yield pigments or, on further sulphonation, dyestuffs (F.P. 754987). Again, chrysene is dinitrated, reduced to diaminochrysene, and then subjected to a double Skraup synthesis to yield a dipyridinochrysene, which is converted to a reddish-yellow cotton dye on oxidation with chromic acid.

A. H. C.

CHRYSIN, 1:3-dihydroxyflavone,



is obtained from poplar buds (Piccard, Ber. 1874, 7, 88; and Darier, *ibid.* 1894, 27, 21). It is a member of the quercitin series (Perkin, J.C.S. 1896, **69**, 1443), and dyes cloth mordanted with aluminium a pure yellow; with chromium, an orange-yellow; and with iron, a pale chocolate (Perkin, *ibid.* 1897, **71**, 818).

CHRYSOBERYL. Aluminate of beryllium, $BeAl_2O_4$, crystallising in the orthorhombic system, and used as a gem-stone. It is usually met with as well-formed crystals, which as a result of twinning often simulate hexagonal forms, or as rolled pebbles in river gravels. Sp.gr. 3·65–3·75; hardness 8½, taking the third place amongst minerals, being exceeded only by diamond and corundum. Few minerals are so resistant to chemical reagents as chrysoberyl; it is not attacked by acids nor fusible before the blowpipe, and is decomposed only by fused alkalis. The colour ranges in various shades of yellow and green. The variety *alexandrite* is emerald-green in daylight, but violet-red in lamplight. Another gem variety, known as *cymophane* or "oriental cat's-eye," shows a bluish milky band of reflected light which travels across the convex polished surface as the stone is moved about. Chrysoberyl occurs embedded in granite and crystalline schists. Material of gem quality comes from Ceylon, Brazil and the Urals. Colourless crystals have been found in the ruby mines in Upper Burma and in the Gold Coast in West Africa. By reason of its high degree of hardness it has occasionally been used for jewelling watch-bearings.

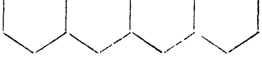
L. J. S.

CHRYSOCOLLA. A hydrated silicate of copper, sometimes of importance as an ore of copper. The formula is usually given as $CuSiO_3,2H_2O$, but the composition is variable, the mineral often being mixed with various impurities—silica, alumina, copper carbonate or phosphate, limonite, etc. On these differences in composition several trivial varieties have been distinguished by special names. The mineral is of secondary origin, occurring in the upper portions of deposits of copper ores. It forms encrusting or botryoidal masses, which may be vitreous and translucent, resembling opal or enamel in appearance, or dull and earthy. The colour ranges from bright green to bright blue, and there is a wide range in the sp.gr., 2·0–2·8. Under the microscope it sometimes shows a minutely fibrous structure, and small acicular crystals from Idaho have been described, but with variable and uncertain optical data and sp.gr. 2·4 (J. B. Umpleby, 1914). Interbanded with the microcrystalline material is often some optically isotropic material, and for this amorphous equivalent of chrysocolla the name *cornuite* has been proposed (A. F. Rogers, 1917).

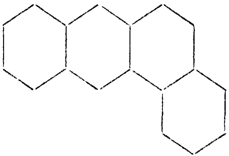
A variety known as *pitchy copper-ore* (Ger. *Kupferpecherz*), dark brown or black in colour and with the appearance of pitch, is of some importance as an ore of copper, particularly in Chile. It consists of a mixture of chrysocolla and limonite (F. N. Guild, Amer. Min. 1929, **14**, 313). Chrysocolla of the more ordinary type has been mined for copper in South Australia, Belgian Congo, Chile, Arizona, Idaho, etc. The name chrysocolla, from χρυσός, gold, and κόλλα, glue, was applied by the ancients to materials used for soldering gold, and included, besides certain copper minerals, also borax.

L. J. S.

CHRYSOGEN. The crude orange-yellow hydrocarbon responsible for the yellow colour and green-yellow ultraviolet fluorescence of crude anthracene. Capper and Marsh (J. Amer. Chem. Soc. 1925, **47**, 2847; J.C.S. 1926, 724) studying absorption and fluorescence spectra, concluded that chrysogen was either naphthacene (I), or 1:2-benzanthracene (II) (*see also* Cook and co-workers, Proc. Roy. Soc. 1932, B, **111**, 469; Morgan, J.S.C.I. 1928, **47**, 132).



I.



II.

Winterstein, Schön and Vetter (Z. physiol. Chem. 1934, **230**, 158) separated chrysogen from anthracene by chromatographic analysis and completely identified it with naphthacene (I).

CHRYSOLITE, a clear, transparent, yellowish green variety of olivine $(MgFe)_2SiO_4$.

CHRYSONAPHTHAZINE *v.* AZINES.

CHRYSOPHANIC ACID (*Chrysophanol*) *v.* CHRYSAROBIN.

CHRYSOPRASE *v.* CHALCEDONY.

CHRYSOTILE *v.* ASBESTOS and SERPENTINE.

CHRYSOTOLUAZINE *v.* AZINES.

CHRYSTOLON *v.* CARBORUNDUM.

CHUFA. Earth almond. The tubers of *Cyperus esculentus* Linn., grown extensively in central and southern areas of the United States. The tubers, which are 0·5–1·0 in. in length, have a nut-like flavour and are said to resemble the water chestnut. They are sometimes roasted and used as a substitute for coffee. The plant is also valued as forage for pigs. The fat content of the tubers averages 20–29%, starch 12–30%, and sucrose 15% (Power and Chesnut, J. Agric. Res. 1923, **26**, 69; Pieraerts, Mat. Grasses, 1924, **16**, 6674; Anon. Giorn. Chim. 1933, **27**, 297).

Baughman and Jamieson (J. Agric. Res. 1923, **26**, 77) record a detailed examination of the oil and give the following characteristics: d^{15} 0·918, refractive index 1·4662 (25°), saponification value 191·3, iodine value 76·89, Reichert-Meissl value 0·2, Polenske value 0·3, acetyl value 4·55, acid value 1·70. The calculated composition of the fatty acids is:

	%
Lignoceric acid	0·3
Arachidic acid	0·5
Stearic acid	5·2
Palmitic acid	11·8
Myristic acid	trace
Oleic acid	73·3
Linolic acid	5·9
Unsaponifiable acid	3·0

A phytosterol, m.p. 134°–135°, was also found. A related species, *C. rotundus*, from Japan, yields 1% of an essential oil which, according to Kimura and Ohtani, contains 32% of cyperene ($C_{15}H_{24}$) and 49% of cyperol ($C_{15}H_{24}O$).

A. G. Po.

CH'Ü-MA *v.* China Grass.

CHURCHITE. A hydrated phosphate of cerium (Ce_2O_3 51·87%) and calcium, occurring as grey fan-like aggregates of acicular crystals encrusting quartz and slate in a Cornish copper lode. Unfortunately nothing is known of the exact locality of the mineral.

L. J. S.

CHYMASE a synonym for Rennet.

CHYMOTRYPSIN. An active proteolytic enzyme obtained by the action of a minute quantity of trypsin on a crystalline protein contained in acid extracts of pancreas (Kumitz and Northrop, J. Gen. Physiol. 1935, **18**, 433). This enzyme hydrolyses casein more slowly than trypsin but carries the hydrolysis further and attacks different linkages.

E. F. A.

CIBACET *v.* Acetate Silk Dyes.

CIBANONE DYES. Blue G, 3G, RA; Black B; Brown B; Olive B; Orange R, CR; Red 4B; Violet BW; Yellow R (*v.* Anthraquinone Dyestuffs.

CICHORIIN, $C_{15}H_{16}O_9$,2Aq., m.p. 213°–215°, $[\alpha]_D$ −104·5°, is the glycoside present in *Cichorium Intybus*, chicory.

It is isomeric with æsculin differing only in the position of the sugar residue.

According to K. W. Merz (Arch. pharm. 1932, **270**, 476), it is hydrolysed to glucose and cichorigenin, $C_9H_6O_4$, which is 6:7-dihydroxycoumarin. In cichoriin the glucose residue is attached to position 7, whereas in æsculin the attachment is at position 6.

When cichoriin is first methylated and then hydrolysed, 6-methoxy-7-hydroxycoumarin, *i.e.* scopoletin, is obtained.

E. F. A.

CICUTOXIN, $C_{19}H_{26}O_3$, the poisonous principle in water-hemlock (*Cicuta vagans*) is contained in the tubers to the extent of 0·3–0·4%. It is found also in *C. virosa*. It is a yellow resin-like substance which readily decomposes and polymerises above 50°, it has d^{22} 0·9659 and n_D^{25} 1·5885. Unites energetically with bromine and ignites spontaneously in contact with strong nitric acid. On dry distillation it yields an oil, $C_{13}H_{21}O_2$, of d^{20} 0·936. Distilled in a current of steam it gives an oil, $C_{14}H_{22}O$, of a pleasant odour and which gradually polymerises to a transparent semi-solid resin. On oxidation with nitric acid cicutoxin yields carbon dioxide, oxalic acid, hydrogen cyanide, *iso*butyric acid, and acetyl-2-*cyclo*pentanone, b.p. 73·5°/15 mm. Compounds of cicutoxin with lead, barium, hydrogen chloride, ammonia, bromine and iodine are known. Cicutoxin appears to be a derivative of 4-pyrone (Jacobson, J. Amer. Chem. Soc. 1915, **37**, 916); it exhibits absorption bands at λ 570–64 and λ 650–680 (Švagr, Chem. Listy, 1923, **17**, 166).

CIGNOLIN, the anthranol of 1:8 dihydroxyanthraquinone (*v.* Chrysarobin).

CIDER or CYDER is a beverage produced from the juice of apples by alcoholic fermentation. A corresponding beverage, perry, is made from the juice of pears; this so closely resembles cider in general type and qualities, methods of production, and centres of manufacture, that for the purpose of this article the two drinks can be treated in common and distinctive reference only made to perry when occasion requires.

Both are beverages of considerable antiquity, the earliest extant mention of cider in this country relating to its production in Norfolk as far back as the thirteenth century. In France it was being made in the sixth century, and probably still earlier. That country and Great Britain are the two leading producing countries at the present time, the output of the former in some years exceeding 400,000,000 gallons and being many times greater than that of the latter. The approximate area of the French cider fruit orchards, centred mainly in Normandy and Brittany, is 1,330,000 acres, and of the English 65,000 acres. The latter are situated principally in the counties of Devon, Hereford and Somerset, with Gloucester and Worcester next in order. Cider fruit and cider production also extend into Dorset, Monmouth and other counties adjacent to those named. In Norfolk and, to a less extent, Kent, cider is also made commercially, but in those districts cider varieties of apples are not grown on any considerable scale and "market" (*i.e.* eating) apples are used instead.

Cider in some form is made in most other countries in which apples flourish, but in their case for the most part vintage varieties of the fruit are not grown. In Europe Germany, Switzerland and Spain particularly have gained some repute for their cider. The beverage produced in the United States and Canada in some quantity under this name has been during recent years mostly unfermented apple juice, although latterly in Canada efforts to develop the manufacture of the fermented article have been vigorously pursued.

The initial definition of cider given above indicates a beverage with a material content of alcohol, and in France in particular the use of the name is protected by law and must only be associated with beverages conforming to certain specified legal standards. Other countries vary in the extent and methods of protection and in some they are practically non-existent. Thus under the general name of cider there are to be found beverages of an extremely wide range of types, differing in respect of original juice content, chemical composition, and form of presentation. In the matter of juice content France, for example, enforces the application of specific forms of name designation indicating (*a*) whether the article is produced from undiluted or diluted juice and, if the latter, (*b*) the degree of dilution.

In England no legal standards have been formulated, but under a regulation of the Ministry of Health, which came into force on January 1, 1927, no preservative except sulphur dioxide is permitted. The maximum content of sulphur dioxide allowed is 0·02%, which is equivalent to 14 grains per gallon. The introduction of a National Mark Scheme for Cider in 1931 by the Ministry of Agriculture and Fisheries has led, however, to the establishment of a voluntary standard for English ciders which must be attained before the ciders are entitled to bear the National Mark. According to this standard, the cider must be made from apples grown in England and Wales. It must be made from either the pure juice of apples or a diluted juice containing not more than 25% of its own volume of a syrup of pure cane or pure beet sugar. The original specific gravity of the juice must not be below 1·040 and the percentage of volatile acid (as acetic) must not exceed 0·3%.

The chemical composition of cider in relation to the contents of alcohol, sugars, acid, and tannin is very variable and is responsible for a series of types of the beverage differing widely in taste and physiological action. Total sugar content determines the classification under the heads of sweet, medium, dry and extra dry, the percentage ranging from 6–7% by weight or over in the case of sweet ciders to below 1% in the case of the extra dry types. Alcoholic strength tends to vary in the opposite direction and may be but little over 2% by weight in sweet ciders and exceeding 5–6% in dry and extra dry: in special cases, where a higher content is required, this generally cannot be obtained directly from untreated pure juices on account of their limited initial sugar content and is provided either through the fermentation of added sugar or by direct fortification with spirit. The latter methods make it possible to secure a high alcohol content, even in the sweeter types. Acid and tannin determine the degree of acidity, and astringency and bitterness, respectively in the flavour. Ciders containing over 0·4% of malic acid rank as brisk ciders and the low-acid types generally range in acidity between 0·2 and 0·4%. A tannin content in excess of 0·2% communicates a definite " bittersweet " character to the flavour and is generally accompanied by at least a fair degree of fullness in body; below that figure this " bittersweet " character is normally not marked on the palate. Ciders of a low-acid, somewhat bittersweet character are generally favoured in France; in Great Britain a brisker, less bittersweet type is in most demand except in the cider-making country districts, where a rougher and more bitter, dry type suits the local taste.

Cider is supplied either in cask or bottle. Draught cider in the wood is usually still or nearly so, any slight sparkling condition being generally the result of a slow after-fermentation. In bottle, sparkling cider is the rule, the carbon dioxide to which the "life" is due being secured mostly by natural conditioning in the bottle or by artificial carbonation prior to bottling. The latter method predominates in commercial production. A third type of sparkling cider is that produced by the true "champagne" method, the liquor being first strongly fermented in bottle and then disgorged to remove all sediment.

Although a beverage coming within the ordinary definition of cider can be made from any kind of apple, the result is likely to be inferior and lacking in commercial appeal unless either the fruit is composed of vintage apples exclusively or of a mixture in which vintage fruit is the predominant constituent, or, alternatively, special methods of treatment are adopted. Fruit falling within the class of " eating " apples, *i.e.* dessert and culinary varieties, is characterised by a deficiency of tannin and, usually, an excess of acidity from the vintage point of view. Cider made therefrom by usual procedure is typically thin, lacking in body and character, more or less oversharp (according to the variety), poor-coloured, and coarse-flavoured as a result of an excessive rate of fermentation of the juice.

Since in practice apples unsuited for dessert or culinary purposes are normally sent to the cider mills, they tend undeservedly to be ranked as vintage fruit. Strictly, that term should be reserved for varieties yielding a juice which by fermentation and after-treatment will produce a cider of good quality in its particular class, irrespective of any blending requirements. Quality in this connection includes characters such as aroma, flavour (in respect of fruit character as distinct from the aspects due purely to sugars, acids, and tannins), body and low nitrogen content. The sum total of such characters may be expressed by the term " vintage quality." A cider apple proper may, therefore, be defined as one normally possessing vintage quality of a satisfactory order.

The individual varieties of cider apples show a very wide range of composition in respect of constituents which are of vintage importance. Sugars, for example, may range from 7 to over 20%, malic acid from 0·1 to over 1·5%, and tannin from 0·1 to over 0·6%. The specific gravity of the juice ranges generally between 1·035 and 1·090. Although not an exact index of the total sugar content of the juice owing to the presence in the juice of other soluble solids, the specific gravity affords a very fair approximation, by far the greatest proportion of the soluble solids being sugars. A juice with a specific gravity of 1·040 usually contains about 8% of total sugar ; of 1·050, approximately 10% ; and of 1·060, approximately 14%.

Cider apples are classified according to the chemical composition of their juice in respect of the amounts of malic acid and tannin normally present. They fall into three main classes—sharp, sweet, and bittersweet.

As a result of the examination of a large number of English cider apples an extended classification enabling varieties to be grouped so that their blending requirements may be closely indicated has recently been prepared by the Long Ashton Research Station, which serves as the research centre for the cider industry in this country.

This classification is as follows:

Sharp Class.—*Group I.*—Full Bittersharp (*Foxwhelp Type*). Varieties with juices normally containing *not less* than 0·75% malic acid and 0·18% tannin.

The members of this group are very acid in taste. Their ciders are too sharp and too much inclined to bitterness for use unblended.

Group II.—Full Sharp (*Frederick Type*). Varieties with juices normally containing *not less* than 0·75% malic acid and *not more* than 0·18% tannin.

Ciders made from these varieties alone are too sharp and generally lack body.

Group III.—Medium Bittersharp (*Kingston Black Type*). Varieties with juices normally containing between 0·45 and 0·75% malic acid and *not less* than 0·18% tannin.

Into this group fall most varieties that yield palatable and well-balanced ciders unblended, Kingston Black being the outstanding example. In some instances and in certain seasons, especially when body is lacking or some trait of flavour is abnormally prominent, blending gives an improved beverage; in such instances they require the addition of an already balanced blend in quantity sufficient to give the character sought for.

Group IV.—Medium Sharp (*Langworthy Type*). Varieties with juices normally containing between 0·45 and 0·75% malic acid and *not more* than 0·18% tannin.

For this group, owing to the low tannin content, blending with " bittersweet " material is generally essential. Only infrequently can blending be dispensed with. Because of the medium acid content the material used for blending needs to be already balanced in respect of acidity.

Ciders made from the varieties of this group unblended, while usually of about the right standard of acidity, generally lack body and sufficient " tannin " character.

Sweet Class. *Group V.*—Sweet (*Sweet Alford Type*). Varieties normally containing *less* than 0·45% malic acid and *less* than 0·18% tannin.

The members of this group are the " sweet " varieties proper. By themselves they generally yield ciders insipid to the palate because of deficiencies of acid and tannin.

Bittersweet Class. *Group VI.* — Mild Bittersweet (*Belle Norman Type*). Varieties normally containing *less* than 0·45% malic acid and between 0·18 and 0·25% tannin.

This group is sufficiently numerous to justify its separation from Group V. It includes a type of variety that is on the border-line between the " sweet " and " bittersweet " classes. While in many seasons chemical analysis places several of them in the " sweet " class, the palate usually ranks them as mild " bittersweets." Their ciders unblended resemble those of Group V, but with rather more character.

Group VII.—Medium Bittersweet (*Knotted Kernel Type*). Varieties normally containing *not more* than 0·45% malic acid and approximately 0·25–0·4% tannin.

This group is closely described by its title " medium bittersweet." Ciders made from its members unblended have that character very definitely marked as well as distinct lack of acidity. The tannin percentage varies considerably with most varieties according to season—this applies to Groups VI and VIII also—and occasionally places them chemically in the Group VI range; but the palate marks them almost invariably as " medium bittersweets."

Group VIII.—Full Bittersweet (*Strawberry Norman Type*). Varieties normally containing *not more* than 0·45% malic acid and *not less* than 0·4% tannin.

Members of this group are pronounced " bittersweets " with the tannin character generally overwhelming to the palate. That feature distinguishes their ciders from those of the Group VII varieties, which otherwise they closely resemble. Not infrequently this character renders it impossible to use them in blends except in low proportions.

While the chemical composition of the apple does not necessarily indicate the value of that apple for cider making, nevertheless vintage quality is closely correlated as a rule with the composition of the juice. Apple juice is a liquid containing many constituents, of which the chief in quantity are the sugars (lævulose, glucose, and sucrose), malic acid, tannins, pectin and minerals. Typical analyses of three varieties of French apple juices are given in the following table:

	Bedan.	St.Martin.	Bouteille.
Density of juice	1063	1060	1055
	%	%	%
Water	83·15	84·34	85·75
Glucose and lævulose	11·10	10·00	9·10
Sucrose	1·40	1·40	1·30
Malic acid	0·28	0·26	0·30
Nitrogen	0·055	0·062	0·064
Tannins	0·15	0·12	0·13
Pectins and Gums	0·32	0·51	0·42
Ash	0·23	0·36	0·34
Unidentified compounds, fats, sorbite, etc.	3·315	2·948	2·596
	100·000	100·000	100·000

The nature of the ash constituents and the approximate quantities of the individual constituents are shown in the table on p. 123, which have been obtained by the analyses of three typical French ciders.

	Ille-et-Vilaine	Manche	Seine-Inf.
	%	%	%
Silica . . .	0·0017	0·0010	0·0020
Phosphoric acid .	0·0229	0·0205	0·0225
Sulphuric acid .	0·0145	0·0065	0·0225
Chlorine . . .	0·0023	0·0020	0·0225
Iron and aluminium oxides . .	0·0017	0·0015	0·0225
Calcium . . .	0·0050	0·0042	0·0100
Magnesium . .	0·0037	0·0080	0·0150
Potassium . .	0·0970	0·0113	0·0730
Sodium . . .	0·0020	0·0021	0·0015
Total ash . . .	1·0805	1·0980	2·0787

Apple tannins have not been very closely studied, but they resemble more the products from coffee, cachou, or quinquina than oak-gall tannin. Their oxidation by means of an oxidase is mainly the cause of the characteristic amber colour of ciders.

The nitrogenous compounds of apple juice consist of complex proteins, acid amides, and traces of ammonia. In freshly expressed juices the nitrogen content usually ranges from 0·15 to 0·03%. During the course of fermentation a material quantity of the nitrogen content is removed owing to its assimilation by the yeasts and the residual amount in most finished ciders is approximately 0·04%. These constituents have an important bearing on the quality of the cider since they are mainly responsible for the rate of fermentation of the juice. If the nitrogen content is high, the fermentation of the juice is rapid and a coarse type of cider results. A low content of nitrogen is associated with a slow rate of fermentation and a product of superior quality.

The composition of the juice of any individual variety is subject to considerable variation, both from year to year and when obtained from samples of fruit grown under different local conditions. Many factors influence its composition. Among these the more important are climate, soil, condition of ripeness of fruit at the time of expression of the juice, methods of culture of the tree, age of the tree, the size of the crops borne by the tree during the previous two or three years, and manurial treatment given to the tree.

Perry pears may be distinguished from other varieties of pears by their possession of superior vintage quality, as in the analogous case of the cider apple already referred to. The same general remarks as regards composition and its liability to variation apply in their case too. Owing to their relatively small number, no systematic classification has hitherto been established. The features of any classification, if formulated, would probably follow along very similar lines to those of the apple classification outlined above.

The possession of high vintage quality does not necessarily entitle the variety in question to a place in a selected list of varieties to be recommended to growers for culture. What may be comprehensively termed the "orchard qualities" of the variety have also to be taken into account for economic reasons. Thus, for a variety to qualify for inclusion in a selected list, it must attain a suitable standard in respect of both vintage and orchard quality. The important characters concerned with the orchard quality of a variety are the capacity of the tree to grow adequately and to maintain a reasonable state of good health over a long period of years under grass orchard conditions, freedom from serious susceptibility to damage from insect pests and fungus diseases, good cropping quality, and individual fruits of at least fair size.

During the past quarter of a century both the vintage and orchard qualities of many varieties of cider apples have been investigated and, as a result, the list on page 124 of approved sorts prepared by the Long Ashton Research Station. Some of the varieties included in the list, such as Kingston Black, Foxwhelp, and Cap of Liberty, need to be grown under suitable local conditions and on appropriate soil, but most of the varieties named can be recommended where local conditions are favourable for apple culture in general.

Cider apples and perry pears are normally grown in grass orchards, the type of tree being that known in horticulture as a "standard," a form with a single main stem at least 6 ft. in length from ground level to the beginning of the head of the tree. This type of tree is necessary to enable use to be made of the grass sward of the orchards for grazing by livestock. Cultivation in grass is preferred to cultivation in tilled land on account of reduced costs of cultivation, the better harvesting conditions for the fruit and the lower nitrogen content obtained in the juice. The individual trees should stand a minimum of 30 ft. apart and many strongly growing varieties need a distance of 35 to 40 ft. apart. An adequate and economic control of pests and diseases can be obtained by spraying in alternate years with an egg-killing winter wash and a spring spraying with lime-sulphur respectively. The sward of the orchard should be kept close by grazing. After the heads of the trees have been suitably shaped and established in their earliest years little pruning is required beyond an annual overhaul to remove any interlacing or dying and dead branches. Orchard management along these lines is now being more and more extensively practised, but the older generation of orchards in the West of England affords many examples of the deplorable results of neglect of proper management.

The earliest-ripening varieties of cider apples begin to ripen in September and the latest are not fit to gather until the early winter. The correct time for harvesting needs to be decided for each variety separately ; it is when the apples fall freely when the tree is lightly shaken. Premature harvesting means a loss of quality in the ultimate cider, since the fruit does not acquire its full vintage quality until it has ripened to a comparatively mature state on the tree. Normally the fruit at this stage of maturity has not yet reached its optimum condition for cider-making and needs to be stored for a period before that point of condition is reached as a result of the conversion of

Harvesting season.	Name of vintage class of variety.		
	Sharp.	Sweet.	Bittersweet.
Early (to mid-October)	Backwell Red	Court Royal	Belle Norman (*syn.* Perthyres) Major Royal Jersey II White Jersey White Norman
Mid-season (mid-October to early November)	Cap of Liberty (*syn.* Red Soldier) Dymock Red Fair Maid of Devon Foxwhelp Frederick Kingston Black Langworthy (*syn.* Sour Natural, Wyatt's Seedling) Porter's Perfection Rejuvenated Foxwhelp Stoke Red Yellow Styre	Berkeley Pippin Eggleton Styre Sweet Alford Sweet Coppin Woodbine II (*syn.* Northwood, Sweet Woodbine)	Bulmer's Norman Ellis' Bitter Knotted Kernel Masters' Jersey (*syn.* Harry Masters' Jersey) Royal Wilding Tremlett's Bitter Yarlington Mill Jersey
Late (November and later)	Crimson King Lambrook Pippin Reinette Obry	Woodbine I (*syn.* Slack-ma-Girdle)	Dabinett Dove Medaille d'Or I Michelin Reine de Pommes Silver Cup Tardive Forestier.

starch to sugars and various changes in the pectin and other constituents. During this period of storage the apples can be kept either under cover or outdoors, provided that in the latter case the lowest layer of fruit in the heap does not rest directly on the ground. If that occurs, there is risk of an earthy taint being acquired and transmitted in due course to the cider. Storage on a bed of straw or rough boarding provides the necessary security against this risk. From the foregoing it follows that it is undesirable to mix in the same heap of fruit apples of widely varying conditions of ripeness. Uniformity of ripeness is essential if the best results are to be obtained.

When the fruit is adjudged to be fit for milling the practice in up-to-date factories is to wash it as thoroughly as possible before passing it on to the mill. This operation of washing is of relatively recent introduction into cider-making routine and serves the double purpose of thoroughly cleansing the fruit and affording a convenient and simple opportunity for the removal of any apples which may have rotted during storage. It has also been found that the subsequent management of the fermentation of the juice is easier and the clarification processes rendered quicker and more thorough.

For the expression of the juice considerable improvements have been introduced in recent years in the nature and construction of the mills and presses and the accessory equipment. Most modern cider mills are of the grater type. These, with their high speed of 2,000 revolutions a minute, are capable of reducing fruit to a very finely divided pulp in a short space of time. A mill of average size can deal with a ton of fruit in 10 minutes or less. Most of the newer presses installed are of the hydraulic type. The milled fruit pulp—the "pomace"—is built up on the bed of the press into a "cheese," as it is technically termed. The accessories used in juice extraction are devised to facilitate the rapid and complete expression of the juice and its free drainage from the "cheese" of pulp. For this purpose a wooden slatted drainage rack is first placed on the bed of the press and on it is laid a netted or open-meshed cloth of cotton or other suitable fibre. In this the pomace is received and spread evenly as far as the edges of the drainage rack until a layer of pomace about 3 ins. in thickness is obtained. The overlapping sides of the cloth are then wrapped over the pomace layer and above this a second rack is placed and the same procedure repeated until a "cheese" consisting of about seven tiers or layers of pomace is obtained. The press is then put in action and in the course of from 15 to 30 minutes the bulk of the available juice is expressed, the individual layers of pomace being compressed so tightly that the drainage racks above and below each are nearly in contact.

It is usual to press the pomace immediately after delivery from the mill, but many old cider makers prefer to allow the pomace to stand in tubs for from 12 to 24 hours before pressing. This maceration was found, when the older types of mills and presses were used, to facilitate the subsequent expression of the juice and was believed also to improve the vintage quality of the liquor. Occasional makers still adopt this practice but, with the modern machinery now widely used, it is doubtful if any advantage is derived from it. With the use of modern equipment it is possible to obtain from 75 to 80% of the original weight of the fruit as juice, if the fruit used is in good condition and at a suitable stage of ripeness. With older types of machines a yield of 70% must be ranked as above the average.

The residual pressed pomace after the expression of the juice in the manner described contains about 70% of its weight in the form of juice which cannot be expressed by a single pressing. Many makers break up the cakes of pressed pomace into a fine state of division by a suitable machine and subject this pulverised pomace to a further pressing. By so doing an additional yield of about 20 gallons of juice per ton of fruit can be obtained. It depends upon the value of the particular juice in question whether or not this second pressing is economic.

With modern equipment and fruit in good condition the average yield of juice per ton of fruit should approximate to 160 gallons.

In France, instead of the juice being expressed in this manner it is sometimes obtained by extraction from the thinly sliced fruit by a diffusion process similar to that used in the beet sugar industry. This method has also been tried by some English cider makers, but has not been generally favoured.

The freshly expressed juice is a turbid liquid, somewhat viscous owing to its rather high pectin content, and ranging in colour from a pale straw tint to a deep amber-brown. Its colour generally can be correlated approximately with its acid and tannin contents, acid tending towards the paler shades and tannin towards the deeper; thus a high-acid low-tannin juice is usually very pale and a low-acid high-tannin one dark, while a high-acid high-tannin sample as a rule is decidedly darker than one of similar acidity but less tannin. Held in suspension in the juice are fragments of fruit tissue of varied size, the amount and character depending to some extent on the state of ripeness of the fruit at the time of milling and largely also on the degree of fineness of milling and the form of construction of the cheese and the kinds of cloths used. The coarser material is removed by straining the juice through a fine-meshed sieve after it leaves the press; but normally sufficient suspended solid matter remains in the juice after sieving to render it desirable to take other steps for its removal, so that the fermentation vessels may be kept in cleaner condition and risks of flavour depreciation due to its presence during fermentation reduced as far as possible. A fair clarification of the juice at this stage is mostly effected in practice by one or other of the following three ways. Centrifuging the juice usually is effective to a high degree, but at present few makers outside the larger factories possess appropriate centrifuges. Effective filtration of the juice would serve, but is difficult to attain, and also very slow, owing to the presence of pectins. A simple method is that of "keeving," which consists in allowing the juice to stand at rest for a period of several days (until fermentation becomes active) in a large open vat. Defecation occurs, most of the suspended matter rising to the surface and forming a more or less dense head easily removable by skimming and the bulk of the remainder sinking to the bottom of the vat to form the lees, which are separable by racking at the appropriate time. The chief drawback to the "keeving" method is the acetic fermentation which invariably occurs, sometimes to a slight or even negligible extent when the juices are prompt in coming into active fermentation, but at others to a degree leaving permanently in the prepared cider a distinct taint of aroma and flavour. To minimise this action keeving at low temperature (35°F.) has been adopted with some success where facilities for chilling are available. The most primitive method of juice clearing is still the simplest and the one to be advised usually when a centrifuge is not available. In this the freshly expressed liquor is placed at once in the fermentation casks and allowed to stand there with the bung open pending the onset of active fermentation. This is associated in its earliest stages with the formation of a thick, sticky head of foam, which as formed carries with it much of the suspended material to the open bung-hole where it is extruded over the sides of the cask. Within a few days generally this phase passes, active fermentation takes charge and then, for the first time, it is desirable to insert in the bunghole a bung fitted with a modern form of vent-tube which permits the evolved carbon dioxide to escape and prevents any atmospheric oxygen reaching the liquor.

After the preliminary clarification of the juice, by whatever method adopted, the fermentation process is allowed to proceed uninterrupted until it has reached the desired point. The great majority of cider makers allow the juice to ferment "naturally," in which case the wild yeasts which occur on the skin of the apple and are washed into the juice during the milling and pressing operations are the active micro-organisms concerned. Other makers, however, control the nature of the fermentation by the use of selected yeasts, cultures of which are added to the freshly expressed juice in quantity sufficient to dominate the fermentation which takes place subsequently. More complete control can be obtained by the pasteurisation of the juice before the addition of the pure yeast culture; but this method is open to the drawback that the pasteurisation of the juice affects its flavour to some extent.

In the natural fermentation several different kinds of yeast are usually concerned. During the course of the production of the beverage three distinct phases in the micro-organism flora, characterised by the predominance of certain yeast types, occur. In the initial stages of fermentation yeasts of the *apiculatus* type are relatively numerous. During the most active stages of fermentation which follow, yeasts of the *cerevisiae, ellipsoideus*, and *Pastorianus* types are predominant. When active fermentation has been completed the residual flora is characterised by the presence of a relatively large proportion of small-celled yeasts of the *Torula* class. At this stage also there is generally an increase in the proportion of bacteria to yeasts, unless the later stages in the production of the beverage are very carefully managed.

Two distinct courses of procedure in connection with the fermentation stage are open to the cider maker. Under the older method the juice is permitted to continue to ferment until active fermentation comes to a natural end. When that point is reached steps are taken to clarify by racking or other methods described below. With this method the ultimate character of the cider as regards sweetness depends only upon the extent to which the natural fermentation of the juice is carried. This varies greatly with different juices and is determined mainly by the content of soluble organic nitrogenous compounds suitable for yeast nutrition in the juice.

The alternative method open to the cider maker is the one of "checked-fermentation," which has for its object the retention of a degree of natural sweetness in the liquor desired by the maker. This necessitates bringing active fermentation to a standstill when the corresponding point of specific gravity is approached. Racking for this purpose is unreliable, although occasionally stoppage of fermentation can be obtained in this way when the nitrogenous content of the juice is exceptionally low. Filtration is far more effective, provided that pulp filters of a fairly modern type are used. The most recent way which has been found to give the maker a high degree of control—as well as other advantages—is to centrifuge the fermented liquor when the desired point of specific gravity has been reached.

In the production of sweet ciders the maker using the "checked-fermentation" method obtains a beverage with a part of the natural sweetness of the apple retained, for which he must rely on the efficiency of his method of checking the fermentation. Under the older method the degree of sweetness left in the liquor at the end of the fermentation is very variable in different cases and generally insignificant in amount; the required sweetness has then to be provided by the addition of sugar. For the production of dry ciders fermentation is allowed to proceed in any case until it comes to a natural end.

At the end of the active fermentation period, whether this has been achieved artificially or not, the liquor is placed in clean, tightly-bunged casks and allowed to mature for a period. For the storage of cider in bulk large reinforced concrete vessels lined internally with glass tiles or an impermeable, tasteless, and odourless material unacted on by cider are being used to an increasing extent and displacing the large wooden vats used hitherto.

Generally the liquor reaches the period when it is sufficiently mature for consumption during the course of the spring following the autumn or winter in which it was made. A longer storage period sometimes gives an improvement in quality, but more usually a cider is at its peak of quality during the late spring and summer of its first season.

Before it is placed on the market for consumption some degree of refining is required. For draught cider a final filtration through a pulp filter is adequate; the same applies to bottled ciders intended for natural conditioning. Since, however, ciders refined in this way are subject to the risk of certain bacterial disorders, such as cider "sickness" and acetification, a bacteria-proof filter has been adopted in recent practice to obtain a sterile beverage; the liquor in that event has to be conditioned for bottling purposes by artificial carbonation.

In bottling cider two methods are generally used. The older method, in which the liquor is allowed to condition itself naturally in the bottle by a slow after-fermentation, is somewhat uncertain in its results and has been largely displaced latterly by the method of artificial carbonation. In the former method cider requires to be bottled at the correct time in its life. This varies according to the individual ciders concerned and considerable experience is required to determine when a given cider has reached the best time for bottling; if bottled too soon, the liquid becomes overcharged with gas and an excessive deposit is formed in the bottle; if bottled too late, little or no after fermentation occurs in bottle, the liquid accordingly remaining flat and being frequently disfigured by the development of "fliers" resulting from the growth of acetic bacteria. As a rule bottling under this method should be done between mid-February and early May in the spring following making. The carbonation process of bottling has the great advantage that the cider can be bottled at any time of the year in condition for immediate consumption, while the problem of deposit does not arise. When ciders which have been sterilised by filtration through bacteria-proof filters prior to bottling are used, all parts of the bottling plant as well as the bottles and corks must be sterilised to prevent re-infection with micro-organisms.

The chemical composition of mature ciders differs considerably in individual cases, the most striking differences being usually in sugar and alcohol content according to whether the product is of the sweet or dry type.

The table on page 127 shows the composition of some typical ciders of various degrees of sweetness and dryness.

Cider is subject to several disorders. Of these the commonest are acetification, sickness, ropiness and oiliness, and discoloration. The first three are directly due to the action of specific bacteria, and the last, in some instances at least, may be indirectly attributable to acid-destroying micro-organisms. In the case of acetification, the "vinegar" fermentation, in which several distinct kinds of acetic bacteria may be concerned, all ciders are attacked unless the liquor is protected at all stages of manufacture and subsequently until consumed. Every juice comes from the press more or less heavily infected with the bacteria in question and exposure to air must be reduced to the lowest

	A	B	C	D	E
Density	1008·5	1003·5	1000·0	1025·0	1019·0
	%	%	%	%	%
Total dry extract at 100°	3·025	2·37	2·06	7·71	6·03
Total sugar	1·67	0·23	0·15	5·53	4·03
Alcohol	3·1	7·5	6·45	3·8	4·6
Volatile acids	0·050	0·05	0·036	0·073	0·074
Fixed acid	0·152	0·675	0·458	0·201	0·229
Tannin	0·041	0·170	0·058	0·208	0·234
Ash	0·175	0·375	0·215	0·248	0·235

practicable minimum, for at no period does cider attain a sufficient alcoholic strength to render it immune from the development of these organisms. The carbon dioxide developed during the active fermentation of the juice forms a natural protectant and the liquor as far as possible should be kept saturated with this gas, by direct addition when necessary, throughout its life. Cider sickness, (the " maladie de la tourne " and " la pousse " of the French), is a violent form of alcoholic fermentation produced by the " sickness " bacillus and apt to attack sweet ciders, whether in cask or bottle, when the temperature rises during the late spring or summer following manufacture. Its onset appears without warning and is generally accompanied by an intensely rapid evolution of carbon dioxide. A characteristic odour and flavour are produced and in course of time usually a dense milky turbidity appears in the liquor in consequence of a chemical action of formaldehyde and other aldehydes formed during the fermentation on the tannin of the cider. Ciders with a malic acid content of 0·5% and over are not often attacked. Storage at the coolest temperature available is recommended for all sweet ciders which have not been passed through a bacteria-proof filter.

Ropiness in cider is similar in character to the corresponding disorder of wines, and oiliness appears to be an incipient or little developed stage. It is not of frequent occurrence, but is specially apt to appear when sugar is added for sweetening purposes. The use of a bacteria-proof filter for the final clarification of cider is probably the most effective method of prevention of this disorder. All sugar syrups used for sweetening should be sterilised before addition, as a precaution against infection from this source.

Discoloration or " blackening " of ciders is an unsightly disorder, but otherwise not actually detrimental to the beverage. The affected liquor turns dark after exposure to air, in bad cases within a few minutes of being poured into the glass for consumption. The discoloration is an oxidation effect and associated with the presence of iron in a certain form in the liquor. The iron contamination is most often acquired from metallic utensils with which the pomace or liquor has been in contact, but certain soils are reputed to yield fruit specially susceptible to the disorder. A relatively high acidity in the cider tends to retard the appearance of blackening and those samples which have had their acidity reduced by the action of acid-destroying bacteria appear to be highly susceptible to the trouble. In some cases enzyme action also may be associated with its development. The use of sulphur dioxide as a preservative gives some measure of protection against its appearance.

During recent years several by-products of the industry of some importance have been developed. In France a considerable proportion of the total output of cider each year is distilled for the production of potable alcohol. " Calvados "—a form of cider brandy obtained thus—has been for many years a well-known by-product of the industry. In some countries cider vinegar (*v.* Vol. I, p. 46*a*) prepared by the controlled acetification of fully fermented ciders is produced extensively and is in considerable demand.

Various uses for the pressed pomace left after the final extraction of the juice have been found. In its fresh state it has some value as a food for livestock, provided that it is not kept so long that acetification to a material amount occurs. The material is now generally dried in suitable drying machines until the moisture content is reduced to approximately 10%. In that form it is perfectly stable and can still be used for stock-feeding purposes, being frequently incorporated with other feeding stuffs of more concentrated food value in compound cattle cakes. Considerable quantities of commercial pectin are extracted from dried pomace at the present time and used in jam manufacture. B. T. P. B.

CIGNOLIN. Dihydroxyanthranol, used in the treatment of various skin diseases (*Bayer Products, London*). B.P.C.

CINCAINE. *iso*Propylhydrocupreine hydrochloride, used as a local anæsthetic (*Howards, London*). B.P.C.

CINCHOMERONIC ACID. Pyridine-3:4-dicarboxylic acid.

CINCHAMIDINE *v.* Cinchona Alkaloids (this vol., p. 162*a*).

CINCHENE *v.* Cinchona Alkaloids (this vol., p. 158*c*).

CINCHOLOIPONIC ACID *v.* Cinchona Alkaloids (this vol., p. 159*d*).

CINCHONA ALKALOIDS. 1. Introduction.—The first recorded instance of the isolation of a crystalline material from an extract of cinchona bark is provided by the " cinchonino " prepared by Gomes of Lisbon in 1810. The basic character of this product

was noted by Houtou-Labillardiere, who told Pelletier and Caventou about it, and thus initiated the investigations of these two French chemists, who showed that Gomes's preparation consisted of two alkaloids, cinchonine and quinine (Ann. Chim. Phys. 1820, [ii], **15**, 292). Since then many other bases have been isolated from cinchona bark, the most recent being *epi*quinine and *epi*quinidine, isolated by Dirscherl and Thron (Annalen, 1935, **521**, 48). The following list includes all the alkaloids which can be regarded as belonging to this group:

Empirical Formula.	Name.
$C_{16}H_{18}ON_2$	Paricine.
$C_{19}H_{22}ON_2$	Cinchonine, cinchonicine (cinchotoxine), cinchonidine.
$C_{19}H_{24}ON_2$	Cinchotine (hydrocinchonine), cinchamidine (hydrocinchonidine), cinchonamine.
$C_{19}H_{22}O_2N_2$	Cupreine.
$C_{19}H_{24}O_2N_2$	Quinamine, conquinamine.
$C_{20}H_{24}O_2N_2$	Quinine, *epi*quinine, quinicine (quinotoxine), quinidine, *epi*-quinidine.
$C_{20}H_{26}O_2N_2$	Hydroquinine, hydroquinidine.
$C_{22}H_{26}O_4N_2$	Chairamine, conchairamine, chairamidine, conchairamidine.
$C_{23}H_{26}O_4N_2$	Cusconine, concusconine, aricine.
$C_{38}H_{44}O_2N_4$	Dicinchonine.
$C_{40}H_{46}O_3N_4$	Diconquinine.
Composition undetermined	Javanine, cuscamine, cuscamidine, cusconidine.

It is doubtful whether these are all well-authenticated single substances, as some of them are amorphous and not too well characterised. The alkaloids paytine and paytamine are sometimes included on the insufficient ground that "Payta" bark (*Aspidosperma sp.*), from which they are obtained, has been used as a febrifuge.

Cinchona bark has a long and interesting history. It is a moot point whether its anti-malarial action was known to South American Indians before the advent of Europeans; among travellers in that region, Arrot (Phil. Trans. 1737–8, **40**, 81) and others are of opinion that it was, while Humboldt and Markham hold that it was not. The first cure of a European was reported by Jussieu and is supposed to have taken place in 1600. About 1638 the Countess of Chinchon, wife of the Spanish Viceroy of Peru, was cured of malaria by the use of the bark, and this event was commemorated by Linnæus in the name *Cinchona*, which he adopted for the genus of plants yielding the drug.

The cinchonas occur on the western side of S. America between 10°N. lat. and 22°S. lat., *i.e.* in parts of Venezuela, Colombia, Ecuador, Peru and Bolivia. Though cinchona bark did not meet with universal acceptance among the medical profession on its introduction into Europe about 1632, its use spread rapidly and the great demand led to ruthless exploitation of the natural forests and by 1850 there were serious prospects of a cinchona famine. By that time the cinchonas had been classified botanically and it was feasible to consider the formation of plantations in other parts of the world. A Dutch expedition under J. C. Hasskarl visited the cinchona regions in 1852 to collect plants and seed of as many cinchona species as possible, and in 1859 similar British expeditions were organised by Sir Clements Markham, whose book, "Peruvian Bark," published in 1880, gives a comprehensive account of the work of these expeditions and of the early history of the bark and its uses.

As a result of these Dutch and British enterprises cinchona plantations were established in Java, India, Ceylon and elsewhere, and at first were most successful in India, but in 1855 Charles Ledger obtained a supply of seed of *Cinchona Calisaya*, half of which was planted in Java and half in India. This species did well in Java, but failed in India, and in the former country proved to be the source of a remarkable strain of trees, named *Cinchona Ledgeriana*, which improved by unremitting investigation on the part of the Dutch planters into the effect of cultural methods on yield of alkaloid, gradually ousted India from the dominant position it seemed likely to take about 1880 and conferred upon Java the virtual monopoly in cinchona production which it enjoys to-day.

There are probably few drugs whose early history has been so fully recorded as that of cinchona, and the reader interested in this part of the subject may be referred to the following sources of information additional to Markham's book already mentioned:

1860.	"Nuova Quinologia of Pavon," John Eliot Howard.
1879.	"Pharmacographia," Fluckiger and Hanbury.
1891.	"Pharmacographia Indica 1891," Vol. II, Dymock, Warden and Hooper.
1908.	"The Commercial Products of India," Watt.
1908.	"Scheikundige Bijdragen tot de Kennis der Java-kina, 1872–1907," van Gorkom.
1922.	Indian Trade Enquiry. Imperial Institute. Report on Cinchona Bark."
1931.	"Notes on the Cinchona Industry." Lecture to the Institute of Chemistry, B. Howard.
1931.	"Proceedings of the Celebration of the Three Hundredth Anniversary of the First Recognised Use of Cinchona," Missouri Botanical Garden, St. Louis, U.S.A.
1932.	"Kew Bulletin of Miscellaneous Information, 1932," No. 1.

So long as the world was supplied with cinchona bark from the natural forests of South America a number of varieties of bark, distinguished by such names as "crown," "red," "yellow," "grey," "soft pitayo," "hard pitayo," etc., were marketed, but with the advent of systematic planting, the commercial varieties have been virtually reduced to "factory bark" derived from *Cinchona Ledgeriana* or hybrids and "red bark" or "druggists' bark" obtained from *Cinchona succirubra*, the first being used for the manufacture of quinine and other cinchona alkaloids, and the second for the production of tinctures, extracts, and other galenical preparations. Various devices have been introduced into the plantations to enhance the yield of bark, to raise its alkaloidal content, and to facilitate harvesting and preparation for export, and information on these points will be found in a paper by D. Howard (J.S.C.I. 1906, **25**, 97). Though the bulk of the world's supply of cinchona bark now comes from Java, small quantities are still obtained from S. America, India, Ceylon and San Thomé, but exports from Jamaica and other British possessions seem to have ceased. There are small plantations in Tanganyika Territory, formed when this colony was German East Africa, from which small quantities have from time to time been exported (Worsley, Bull. Imp. Inst. 1935, **33**, 14).

It is of interest to compare the yield and nature of the alkaloids obtained from the old S. American barks with those of modern plantation bark, and that is possible owing to the existence of a few analyses made by modern methods on authentic specimens of old barks, which have been kept as museum specimens. These are included in Table I. For commercial and industrial purposes it is sufficient to determine the moisture, total alkaloids, and quinine content of cinchona bark. For that reason modern analyses recording the proportions of the four chief alkaloids for a particular cinchona bark are rare, but such as have been found are also included in Table I.

TABLE I.

Number.	Date of supply of bark.	Variety of bark.	Total alkaloids. %	Quinine. %	Quinidine. %	Cinchonidine. %	Cinchonine. %	Amorphous alkaloids. %
1	1870	*C. officinalis* (crown bark)	5·48	3·09	0·14	1·34	0·32	0·59*a*
2	1870	*C. pitayensis* (hard pitayo)	6·66	2·42	0·82	0·19	0·98	2·25*a*
3	1870	*C. Calisaya* (yellow bark)	4·12	2·00	0·20	0·46	0·56	0·90*a*
4	1865	*C. Calisaya* (yellow bark)	5·80	3·61	0·16	0·75	0·34	0·93*a*
5	1914	*C. Ledgeriana*	9·10	7·92	0·08	0·10	0·08	0·91
6	1919–1923 (average)	,,	6·13	4·14	0·17	0·54	0·38	0·88*b*
7	1925	,,	5·79	4·14	0·44	0·36	0·25	0·60*c*
8	1925	Hybrid bark	4·54	2·87	0·34	0·33	0·46	0·54*c*
9	1888	*C. succirubra* (red bark)	6·25	1·40	—	2·25	1·92	0·68*d*
10	1921	,,	6·07	1·14	—	1·43	1·73	1·76*e*
11	1930	,,	6·29	2·05	0·11	1·47	1·41	1·25*f*
12	1930	*C. robusta*	5·86	2·01	—	2·42	0·12	1·31*f*

(*a*) These analyses are from records of John Eliot Howard and the results must be accepted with reserve, as at the dates mentioned the methods of separation of the different alkaloids were very rudimentary.

(*b*) Howard, Trans. Roy. Soc. Trop. Med. Hyg. 1924–25, **18**, 358. Average composition of Java bark, 1919–23.

(*c*) Gage, *ibid.*, p. 350.

(*d*) Hooper, " Year-book of Pharmacy," 1888, p. 430.

(*e*) Howard and Chick, *ibid.* 1923, p. 637.

(*f*) Barks from Tanganyika examined by Worsley, Bull. Imp. Inst. 1935, **33**, 22.

Comparison of these analyses establishes the superiority of Calisaya bark, even in 1865, as a source of quinine, and analyses Nos. 5 and 6 indicate clearly that Dutch care of its lineal descendant, *C. Ledgeriana*, has improved the yield of alkaloids, the proportion of quinine present, and, what is equally important, has effected a reduction in the proportion of cinchonidine, the alkaloid which persistently accompanies quinine, and whose control is the principal objective of most pharmacopœial tests for impurities in quinine sulphate.

In the early days of cinchona planting, attempts were made, especially by de Vrij in Java, to popularise the total alkaloids of the bark as an anti-malarial drug, but the rapidity with which the discovery of quinine was followed by the manufacture of this alkaloid in France and England, coupled with the persistent advocacy by Moens in Java of cinchona cultivation for quinine production, soon secured for quinine a dominant position as compared with the other cinchona alkaloids, which it still occupies and is likely to retain. Analyses Nos. 7 and 8 relate to " ledger " and hybrid barks produced in India, where these barks are still grown to meet the needs of the Government quinine factories in Madras and Bengal, which, however, also use considerable quantities of Java bark. The two analyses Nos. 9 and 10 serve to illustrate the striking difference in the relative proportions of the various cinchona alkaloids in *C. succirubra* bark as compared with ledger and hybrid barks.

No. 9 is described by Hooper as that of a typical red bark, being the average of analyses of a large number of Indian-grown samples. No. 10 is an analysis of an average red bark of Indian origin. Nos. 11 and 12 are barks from Tanganyika Territory. Partial analyses of "ledger," hybrid, and succirubra barks from Tanganyika Territory have been made by the Imperial Institute (Bull. Imp. Inst. 1918, **16**, 387; 1920, **18**, 22), by Greenish and Corfield ("Year-book of Pharmacy," 1923, p. 652), and by Goodson and Henry (Pharm. J. 1930, **124**, 351), and complete analyses by Worsley (*l.c.*), who also gives an account of the progress and working of these plantations since 1918.

As a matter of historical interest, it may be recorded that in the late nineteenth century a considerable quantity of cuprea bark was sold in the London market. This bark was obtained from *Remijia pedunculata*, a near relative of the cinchonas, and was remarkable in containing quinine and the corresponding phenol cupreine; some cinchonine and quinidine were also present, but no cinchonidine.

2. Extraction of Alkaloids.—The descriptions of processes quoted below refer both to extraction of the alkaloids for the purposes of analysis and as a first step in manufacture. The underlying principles are the same for both objectives. The alkaloids occur in the bark in combination with acids, and it is necessary to liberate them from these natural salts in order to facilitate extraction by immiscible solvents such as ether, chloroform, benzene, or petroleum. The first step, therefore, is to grind the bark finely, usually to a powder that will pass a sieve with 40 meshes to the linear inch. This powder is then moistened and mixed with an alkali, usually lime or soda-lime, and left to stand until the action is complete, after which the mixture is dried, reground if necessary, and extracted with the selected solvent.

Zebel (Chem.-Ztg. 1891, **15**, 735) describes the commercial process thus: The finely powdered bark is ground to a thin paste with lime, sodium hydroxide or sodium carbonate, and extracted with warm paraffin oil. On standing the oil separates, when it is run off and shaken with dilute sulphuric acid; this acid solution is boiled, and while boiling is neutralised, to litmus paper, with sodium carbonate. Quinine sulphate crystallises out on cooling, while cinchonidine, cinchonine, and quinidine remain in solution as sulphates. The quinine sulphate is purified by recrystallisation from water after treating with animal charcoal. The mother-liquor containing the other alkaloids is treated with sodium hydroxide and the precipitate of quinidine, cinchonidine, and cinchonine extracted with dilute alcohol, which dissolves the first two, leaving cinchonine behind; the two former can then be separated by means of their neutral tartrates, that of quinidine being considerably the more soluble.

Landrin (Compt. rend. 1889, **108**, 750) gives the following description of a small-scale extraction: 300 g. of bark are powdered and passed through a No. 40 sieve, then mixed thoroughly with 1 litre of milk of soda-lime containing 75 g. of quicklime and 75 g. of solution of sodium hydroxide (sp.gr. 1·375). To this mixture, diluted if necessary by adding a little water, 2 litres of petroleum are added, heated to 100° for 20 minutes, with constant agitation; the oil is then decanted, and the extraction repeated with a second 2 litres. The 4 litres of extract are washed twice with 75 c.c. of 10% sulphuric acid added to 150 c.c. of water; and a third time with one-third of these quantities.

A recent example of a small-scale extraction of "ledger" and hybrid bark in Tanganyika Territory is quoted by Worsley (*l.c.*).

Schwyzer ("Die Fabrikation der Alkaloide," Springer, Berlin, 1927) provides a detailed account of a small-scale extraction and a full account of factory operations with diagrams of plant (*see also* Vetter, Festschrift E.C. Barell, Basel, 1936, 541).

The following general processes may be quoted as typical of extraction methods for analytical purposes. The reagents mentioned are those prescribed in the pharmacopœias, which must be consulted for particulars as to strength, etc. The "British Pharmacopœia," 1932, proceeds as follows: 10 g. of bark in about No. 60 powder are thoroughly mixed with 7·5 c.c. of strong solution of lead subacetate diluted with 12·5 c.c. of water, and set aside for 1 hour; 50 c.c. of ammoniacal alcohol are then added, the whole again mixed and left standing for 1 hour. The preparation is next transferred to a continuous extraction apparatus, where, with a little more of the ammoniacal alcohol, it is extracted for about 4 hours. The bulk of the alcohol is removed from the extract, 10 c.c. of *N*-sulphuric acid and 40 c.c. of water added, the mixture heated to boiling, then allowed to cool and filtered through a tight plug of cotton wool, previously wetted, into a separating funnel. The residue in the flask is treated with 15 to 20 c.c. of boiling *N*/10-sulphuric acid, and the acid extract, after cooling, also filtered into the separator. The flask and the cotton wool plug are finally washed with cold water, acidified with dilute sulphuric acid, until alkaloids are completely extracted. 20 c.c. of chloroform are now added to the separator, the contents shaken thoroughly, and the chloroform run off into a second separator and any alkaloids removed from it by agitation with 5 c.c. of *N*-sulphuric acid diluted with 15 c.c. of water, the chloroform being then rejected and the acid extract used to treat in the same fashion two further extractions, each with 20 c.c. of chloroform, of the contents of the first separator. This final acid extract is transferred to the first separator, excess of dilute solution of ammonia added, and the alkaloid completely extracted with successive quantities of chloroform. The combined chloroform extracts are washed with a little water, the solvent distilled off, and the last traces of chloroform removed by dissolving the residue in 5 c.c. of 95% alcohol, which is then evaporated, and the residue dried at 100° and weighed.

The following is a summary of the process prescribed in the "United States Pharmacopœia," 11th Rev. (1936). 5 g. of bark in fine powder and 15 c.c. of 3% hydrochloric acid are heated in a 500 c.c. flask on a water-bath for 1 hour. To the cooled mixture 200 c.c. of ether-chloroform solution (chloroform 1, ether 3) and 10 c.c. of the stronger ammonia test solution are added; the well-stoppered flask is shaken mechanically for 1 hour, left standing overnight, and again shaken for half an hour next morning. The drug is then allowed to settle, 160 c.c. of the clear ether-chloroform liquor, representing 4 g. of drug, transferred to a separator, and the alkaloids completely extracted with 5% sulphuric acid. The acid solution is made strongly alkaline with ammonia test solution and the liberated alkaloids extracted with chloroform. The solvent is distilled off in a tared flask and the residue dried at 100° and weighed. The weight multiplied by 25 gives the percentage of alkaloids in the bark.

The "British Pharmacopœia," 1932, specifies for the manufacture of galenical preparations the bark of *C. Calisaya* Weddell, *C. Ledgeriana* Moens, *C. officinalis* Linn., *C. succirubra* Pavon, and hybrids of either of the last two with either of the first two. The bark must contain not less than 6% of alkaloids, of which not less than half must consist of quinine and cinchonidine. The total alkaloids are estimated by the "British Pharmacopœia," 1932, process described above. In the total alkaloids so obtained "quinine and cinchonidine" are estimated together by precipitation as the mixed tartrates, from which the bases are recovered and weighed as such. Two examples of the tartrate precipitation process are given below and it is, therefore, unnecessary to describe in detail the "British Pharmacopœia" method as used for the total alkaloids of the bark.

The "United States Pharmacopœia" (11th Rev., 1936) prescribes the dried bark of the stem or root of *C. succirubra* or its hybrids, or of *C. Ledgeriana* and *C. Calisaya* or hybrids of these with other *Cinchona* spp. The bark must contain at least 5% of alkaloids as estimated by the "United States Pharmacopœia" process described above.

The "German Pharmacopœia," 4th ed., 1926, specifies the bark of *C. succirubra*, and requires it to contain 6·5% of alkaloids calculated as quinine and cinchonine (mean mol. wt. 309·2) and determined by titration of the extracted total alkaloids with methyl red as indicator.

3. ANALYTICAL (*a*).—**Estimation of Individual Alkaloids.** The pharmacopœial methods described above are not only examples of processes for the extraction of cinchona alkaloids, they also provide modes of estimating the total alkaloids in a sample of bark. In the total alkaloids so extracted it is nearly always necessary to estimate quinine, or quinine and cinchonidine, and sometimes each of the four chief alkaloids. It must be remembered that the estimation of one component in a mixture of organic substances can rarely be effected with the accuracy characteristic of the majority of determinations of constituents of inorganic mixtures. Of the numerous methods that have been devised for dealing with mixtures of cinchona alkaloids, probably the best is that of Howard and Chick with a slight modification introduced by Chick (Allen's "Commercial Organic Analysis," 5th ed., vol. VII, p. 426). This method has the advantage that it provides an estimate of the possible yield of quinine sulphate from a bark, but it should be realised that when this method is applied to the total alkaloids of two barks, such as No. 5 and No. 9 in Table I, the quinine sulphate from No. 5 will contain less cinchonidine sulphate than that from No. 9. Goodson and Henry (Pharm. J. 1930, **124**, 351 ; Quart. J. Pharm. 1930, **3**, 238 ; 1932, **5**, 161) have examined the "quinine sulphate," "cinchonidine tartrate," "quinidine hydriodide," and "cinchonine" obtained in the application of this process to certain mixtures of cinchona alkaloids, differing materially from those characteristic of the total alkaloids of "factory" bark and have shown that in such cases the precipitates obtained need examination. Howard and Chick also point out in the description given below that the quinine sulphate obtained is not to be regarded as pure. The method does, however, give good results in skilled and experienced hands, and the inexperienced, before attempting it, should practise the process on cinchona alkaloid mixtures of known composition.

To obtain satisfactory results by Howard and Chick's method a quantity of alkaloid of about 5 g. should be available. It is desirable to start the assay with the estimation of the total alkaloids, as this simplifies the subsequent work and the result is a useful check on the estimation of the individual alkaloids. For this purpose it is only necessary to evaporate to constant weight the extract obtained by any of the methods described under the previous heading; or, in the case of the paraffin and sulphuric acid extraction, to make alkaline with sodium hydroxide, wash out with chloroform, evaporate to dryness, and dry to constant weight at 100°–110°. Having obtained the weight of total alkaloids, add 3 c.c. of 10% sulphuric acid for every gram of alkaloid, and warm on the steam-bath till completely dissolved. Then add 80 c.c. of distilled water for every gram of alkaloid, boil, and while boiling neutralise exactly to litmus paper with dilute ammonia solution (10%). On cooling for 2 or 3 hours with occasional stirring practically the whole of the quinine will crystallise out as sulphate, owing to its being almost insoluble in ammonium sulphate solution. Filter through counterpoised filter papers on the filter-pump, press the crystals down well, pumping as dry as possible, and following with two washes of cold water each about equal in volume to the bulk of the precipitate. The filter papers and crystals are now dried to constant weight at 100°. The weight of anhydrous quinine sulphate found multiplied by 1·18 gives the amount of rough hydrated quinine sulphate, or by 0·868 the amount of rough quinine alkaloid. This quinine sulphate is neither white nor pure, being usually contaminated with colouring matter and cinchonidine sulphate, and requires further treatment. But with the present-day Ledgeriana barks the weight may be taken as representing the true amount of quinine sulphate, as in some thousands of analyses of this bark by B. F. Howard and O. Chick, the amount of quinine sulphate left in the mother liquor almost exactly compensated for the impurities in the crystals weighed.

To the mother liquor and washings from the crystals add about 20 g. of Rochelle salt dissolved in 30 c.c. of hot water, and stir occasionally during 2 or 3 hours. Cinchonidine is completely precipitated as tartrate. This is collected on counterpoised filter papers at the pump, washed with three lots of cold water each about equal in bulk to the precipitate, which is then dried and weighed. This weight, multiplied by 0·797, gives the cinchonidine alkaloid. Should the bark contain very little cinchonidine, and no tartrate be obtained after standing 3 hours, it is best to leave the solution for a full 24 hours to ensure complete precipitation.

The filtrate is made alkaline with sodium hydroxide solution and shaken out three times with ether, using 100 c.c. of washed ether each time. The combined ethereal extracts are in turn extracted with three lots of 10% sulphuric acid using 10, 10, and 5 c.c. respectively, and the acid liquids transferred to a separator containing 25 c.c. of ether. Sufficient sodium hydroxide solution is then added to render the liquid distinctly alkaline and the whole well shaken and left to stand 1 hour. Cinchonine crystallises out and is collected by filtration. The aqueous layer is shaken out twice more using 25 c.c. of ether each time. The crystalline cinchonine is washed with the second lot of ether, then dried and weighed, and 0·08 g. added to correct for the solubility of the alkaloid in ether. The combined ethereal liquids are extracted with acetic acid, the extract neutralised at the boiling-point with 10% ammonia solution, using sensitive litmus paper as an indicator, 5 g. of solid potassium iodide added, and the liquid allowed to cool and left 2 to 3 hours to enable the quinidine hydriodide to separate. The clear supernatant liquid is decanted through counterpoised filter papers, the precipitate is warmed with a little 50% alcohol to dissolve amorphous alkaloidal hydriodides, the whole being then filtered and the precipitate washed with small measured amounts of 50% alcohol until the quinidine hydriodide is pale yellow in colour. The precipitate is dried, weighed, and 0·0008 g. added to the weight for each c.c. of 50% alcohol used. The corrected weight multiplied by 0·717 gives the amount of quinidine alkaloid present. The filtrate is evaporated nearly to dryness with the addition of enough dilute sulphuric acid to keep the remaining bases in solution, transferred to a separator, made alkaline, and the amorphous bases extracted three times with ether using 25 c.c. each time. The ethereal extracts are evaporated to dryness and the residue weighed as amorphous alkaloids.

Totaquina.—Estimation of the components in mixtures of cinchona alkaloids has assumed greater importance owing to the introduction by the Malaria Commission of the League of Nations of "*totaquina,*" defined as containing at least 70% of crystalline alkaloids of which not less than 15% must be quinine, with not more than 20% of amorphous alkaloids, and moisture and mineral matter not more than 5% each. The "British Pharmacopœia," 1932, has modified this definition to "totaquina is a mixture of alkaloids from the bark of *Cinchona succirubra* Pavon, *Cinchona robusta* Howard, and other suitable species of *Cinchona.* It contains not less than 70% of crystallisable cinchona alkaloids, of which not less than one-fifth is quinine." Totaquina may be made either by extracting the total alkaloids of a suitable cinchona bark (Type A) or by using the residual alkaloids left in quinine factories after the bulk of the quinine has been extracted, sufficient quinine being added to bring the product up to the required standard (Type B). These two types of totaquina differ considerably in composition, but the pharmacopœial process is designed to deal with both.

"*British Pharmacopœia*" *Method for Totaquina.*—A mixture of 2 g. of totaquina with 20 c.c. of *N*-sulphuric acid, 40 c.c. of water, and 40 c.c. of 95% alcohol is heated to boiling and, while still hot, made just alkaline to litmus by addition of *N*/10-sodium hydroxide. To the cooled liquid *N*/10-sulphuric acid is added drop by drop until the solution is slightly acid to litmus: the liquid is then boiled for 1 or 2 minutes, cooled, and rendered slightly acid to litmus if necessary, boiled, and filtered into a tared flask, the original vessel and filter being washed with boiling water until all the alkaloid is extracted. The washings are added to the filtrate, which is then evaporated to about 120 g.; 30 g. of powdered Rochelle salt are added, the mixture shaken to complete solution and set aside for 24 hours. The precipitated tartrates are collected on a hardened filter, the flask and filter being washed with 80 c.c. of a 20% (weight/volume) solution of Rochelle salt used in suitable portions. The filter and washed precipitate are returned to the flask, shaken with 40 c.c. of solution of sodium hydroxide and 80 c.c. of chloroform and set aside, with occasional agitation, until complete solution is effected. The chloroform solution is then separated, the flask and the aqueous liquid being washed with chloroform in portions until all the alkaloids are extracted. The combined chloroform solutions are washed with a little water, the solvent evaporated, the last traces being removed by dissolving the residue in 5 c.c. of alcohol, which is then evaporated, the final residue being dried and weighed as quinine and cinchonidine. In this residue the amount of quinine is estimated by a methoxyl determination using 0·2 g.; 1% of methoxyl is taken as equivalent to 10·45% of quinine. The procedure for the estimation of cinchonine and quinidine in the filtrate from the quinine and cinchonidine tartrates is substantially that of Howard and Chick described above, and the sum of the percentages of these four alkaloids found is taken as the percentage of crystallisable alkaloids.

Instead of estimating quinine and cinchonidine by either of the two processes described above, the two alkaloids may be precipitated together as tartrates and the content of each determined polarimetrically. This plan forms part of the following process devised by Howard as particularly suitable for cinchona febrifuge (*see* Quinetum), and also for totaquinas of type B, and was adopted as an alternative method by the

Committee of Experts appointed by the Malaria Commission of the League of Nations to investigate the standardisation of totaquina (CH/Malaria 183, Geneva, 10/10/1932).

Committee Method for Totaquina.—Ten grams of the product are dissolved in 50 c.c. of 10% hydrochloric acid, the solution being transferred to a large separator containing 750 c.c. of washed ether. Excess of ammonia solution (sp.gr. 0·959) is added and the mixture shaken vigorously. The crude cinchonine which remains undissolved is filtered out at the pump, the filtrate separating into two layers, (*a*) ethereal, which is returned to the first separator, and (*b*) aqueous, which is placed in a second separator, where it is re-extracted with another 500 c.c. of ether, which is added to the first lot, the aqueous liquid being reserved for further treatment. The crude cinchonine is washed, first with 50% alcohol and finally with acetone, until the washings in each case come through nearly colourless, after which it is dried and weighed. The washings are evaporated to dryness and the residue of amorphous alkaloids weighed. The combined ethereal solutions are washed out three times with 5% tartaric acid solution using 100 c.c., 50 c.c., and 20 c.c. consecutively; the united acid liquids are heated to boiling, neutralised to litmus paper with 20% sodium hydroxide solution, set aside for 18 hours to allow complete precipitation of quinine and cinchonidine tartrates, and the precipitate collected, washed with as little cold water as possible, dried, and weighed. In it quinine and cinchonidine are determined polarimetrically by the method described below.

The filtrate is transferred to a separator, excess of 10% ammonia solution added, and the mixture extracted twice with ether using 500 c.c. each time. The aqueous liquid is added to the original aqueous liquor already reserved. The combined ethereal solutions are extracted three times with 2·5% sulphuric acid using 80, 40, and 30 c.c. consecutively; these acid extracts are mixed, rendered alkaline with 10% ammonia solution, shaken vigorously with 50 c.c. of washed ether, and the mixture left standing 24 hours to allow a further quantity of cinchonine to crystallise out, which is collected, dried, weighed, and the weight added to that of the cinchonine already isolated. The filtrate is shaken out with two further lots of ether, 500 c.c. each, and the aqueous liquid added to the two aqueous liquors already reserved. The united ethereal extracts are then shaken out three times with 2·5% sulphuric acid using 50, 40, and 30 c.c. consecutively; the mixed acid extracts are heated to boiling, neutralised to litmus with 20% sodium hydroxide solution, excess of powdered potassium iodide, about 10 g., added, and the solution left standing overnight. The liquid is then poured off and added to the reserved aqueous liquids; the precipitate is well stirred with 20 c.c. of 50% alcohol and the mixture warmed to about 50°C. to dissolve amorphous hydriodides. The quinidine hydriodide is then filtered off, washed as economically as possible with warm 50% alcohol until apparently free from amorphous hydriodides, then dried and weighed. The weight multiplied by 0·717 gives the amount of quinidine base.

The bulk of the alcohol is evaporated from the filtrate, the residue of the latter added to the alkaline liquors already reserved, and the whole extracted with a mixture of benzene and amyl alcohol (3:1) ("British Pharmacopœia," 1914). This extract is then evaporated to dryness and the weight of the amorphous alkaloids left added to that found in the initial extraction to give the total amorphous alkaloids.

Polarimetry of Tartrates.—If the precipitate of tartrates of quinine and cinchonidine is too dark-coloured to be used as such for polarimetric reading, it is recrystallised by the following process: About 0·8 g. of the precipitate, dried at 90° to 100°, is mixed with 15 c.c. of a cold, saturated, aqueous solution of quinine and cinchonidine tartrates, 1·5 g. of tartaric acid added, and solution effected by boiling, 0·02 g. of decolourising carbon being added. The solution is then filtered, about 5 c.c. of a cold, saturated, aqueous solution of quinine and cinchonidine tartrates being used to wash the carbon on the filter. The filtrate is raised to boiling-point and at that temperature neutralised to litmus by sodium hydroxide solution and set aside with occasional stirring. The purified tartrate precipitate is filtered off, washed with 3 lots each of 5 c.c. of cold, saturated, aqueous solution of quinine and cinchonidine tartrates, then with 5 c.c. of distilled water and finally dried at 90° to 100°C. and weighed.

For the polarimetric determination 0·5 g. of the purified tartrate is dissolved in 5 c.c. of *N*-hydrochloric acid, made up to 20 c.c. at 17°C. with distilled water and the optical rotation read in a 2 dcm. tube. Pure quinine tartrate under these conditions gives a reading of −10° 50′ and each decrease in this readiug of 2° 65′ represents 1% of cinchonidine tartrate. The weight of tartrate × 0·80 = weight of free alkaloid.

(*b*) **Examination of Commercial Quinine Salts.**—Most pharmacopœias specify standards for quinine salts and prescribe tests with which the salts must conform. The principal impurities to be dealt with are cinchonidine and hydroquinine. The latter is not of practical importance as it is now well established that hydroquinine is at least as effective in the treatment of malaria as quinine, and as it is more costly it is not likely to occur in quinine in abnormal quantities. Much labour has been expended in devising methods for the detection of other alkaloids, and particularly cinchonidine, in quinine sulphate.

Kerner's Test.—Many of these tests are of little more than historical interest and most pharmacopœias now rely upon either Kerner's test or a polarimetric test to ensure the absence of an undue proportion of cinchonidine. Kerner's test (Z. anal. Chem. 1862, **1**, 150; Arch. Pharm. 1878, **14**, 438; 1887, **25**, 712, 749) depends upon the fact that quinine sulphate is the least soluble of the sulphates of the cinchona bases; and that quinine is the most soluble of the common cinchona bases in dilute ammonia. When 2 g. of pure quinine sulphate is shaken with 20 c.c. of water at 60° for some time, and then cooled to 15° for at least half an hour, to prevent supersaturation, it gives a filtrate which precipitates with aqueous ammonia (sp.gr. 0·959), the precipitate just redissolving when 4·3 c.c. of dilute ammonia solution have been added. Quinine sulphate containing any of the other cinchona sulphates, when treated in this manner, requires more ammonia to give a clear solution ; and by this means some idea of the purity of the quinine sulphate is obtained. The details of the test as prescribed in different pharmacopœias vary considerably, and there has been much discussion as to the best form. Quinine sulphate containing about 5% of cinchonidine and hydroquinine sulphates will require between 6 and 7 c.c. of ammonia, while one containing about 10% of these impurities will require about 10 c.c. Points to be noticed in applying the test are that the weights of quinine sulphate and water taken do not, within reasonable limits, affect the result ; the solution should be cooled gradually to 15°, but not below, and retained at that temperature for not less than 30 minutes; the filtration should be rapid and the mixing carefully done by gently rotating and tilting the testing tube, otherwise clotting of the precipitate may take place and a false result be obtained. This test is greatly influenced by the presence of free quinine, when the result may be much in excess of that required for a neutral sulphate of the same degree of purity (D. Howard, Pharm. J. 1896, [iv], **3**, 505) ; and also by the presence of alkaline sulphates, which make it appear purer than it is (Tutin, Pharm. J. 1909, [iv], **29**, 606). These points should be ascertained by testing the filtrate for neutrality with litmus paper, and by evaporating 5 c.c. to dryness and constant weight when the residue should not weigh more than 0·008 g., showing the absence of soluble inorganic salts (Biginelli, Monit. Scient. 1908, **22**, 175). Should the cooling of the mixture be carried out above 15° a larger amount of ammonia will be required, and between 15° and 20° a correction of 0·5 c.c. of ammonia for each degree above 15° may be applied.

The following is the form of this test adopted in the " British Pharmacopœia," 1932. 1 g. of quinine sulphate, which has been dried at 50° for 2 hours, is boiled with 30 c.c. of water for 1 or 2 minutes under reflux in a 100 c.c. resistance-glass flask. The flask is cooled to 15° by means of water at 15°, then corked, shaken vigorously, and kept at 15° for 30 minutes with frequent shaking. The contents are filtered rapidly through a filter-paper 8 to 10 cm. in diameter. 5 c.c. of the clear filtrate are transferred to a test-tube ; to this are added all at once 6·5 c.c. of a solution of ammonia, which must contain not less than 10% (w/w) and not more than 10·2% (w/w) of ammonia, and have a temperature of 15°. The contents of the tube are then mixed gently without shaking. A clear liquid should be produced at 15°.

The " United States Pharmacopœia " (11th Rev., 1936) prescribes the following form : Shake 1·8 g. of quinine sulphate, which must be neutral or faintly alkaline to litmus paper and have been dried at 50° for 2 hours, with 20 c.c. of distilled water at 65° for 30 minutes, cool to 15° and set aside at this temperature for 2 hours with occasional shaking. Then filter through a filter-paper of 8 to 10 cm. diameter and transfer 5 c.c. of the clear filtrate at 15° to a test-tube and mix it gently (without shaking) with 6 c.c. of ammonia test solution containing not less than 10% and not more than 10·2% of ammonia ; the ammonia solution must also have a temperature of 15° and be added all at once ; a clear liquid should be produced.

Kerner's test is designed for use with quinine sulphate and in order to apply it to any other salt of quinine, that salt must be converted into neutral quinine sulphate without change in the composition of the base. Until recently the methods of achieving this conversion left much to be desired. The much-improved method adopted in the " British Pharmacopœia," 1932, may be summarised as follows, using the case of quinine hydrochloride, $B{\cdot}HCl,2H_2O$, as an example.

Quinine hydrochloride (1·2 g.) is dissolved in water (50 c.c.) containing dilute sulphuric acid (5 c.c.). Dilute ammonia solution (5 c.c.) is added and the mixture extracted successively with 30 and 20 c.c. of chloroform. Each chloroform solution is shaken twice with water, using 10 c.c. each time, and using the same water for both lots of chloroform. The mixed chloroform solutions are at once evaporated quickly on a water-bath, most, but not all, of the chloroform being removed. The last traces of chloroform are removed by dissolving the residue in 3 or 4 c.c. of absolute alcohol and again evaporating quickly on a water-bath, with the help of a current of air, until a white opaque residue is obtained. This is dissolved in 20 c.c. of alcohol, 20 c.c. of water added, and 1 c.c. of a 0·02% (w/v) solution of methyl red in alcohol (90%). The solution is heated to 75° and at that temperature *N*/5-sulphuric acid is carefully added, until the colour matches that of a solution at 20° prepared by mixing 56 c.c. of the "British Pharmacopœia" solution of p_H 5·44 with 1 c.c. of a 0·02 solution (w/v) of methyl red in alcohol (90%). In this neutralisation process only acid must be used and any necessity for the addition of alkali must be avoided. The neutral liquid is then evaporated to dryness in a porcelain or resistance-glass dish on a water-bath, and the dry residue powdered and used for the Kerner test as described above.

In the " United States Pharmacopœia " (11th Rev.) the mode of application of the Kerner test to quinine base and salts, other than the sulphate, is varied. Quinine base is neutralised to sulphate by dissolving 1·5 g. of the base dried at 100° in alcohol (25 c.c.) and hot water (50 c.c.), adding enough *N*-sulphuric acid (about 5 c.c.) to make the solution acid, and then titrating back to neutrality with *N*-sodium hydroxide, using methyl red as indicator. For the acid sulphate 2·52 g. of the salt $B{\cdot}H_2SO_4,7H_2O$ is neutralised to methyl red with *N*-sodium hydroxide solution. With quinine dihydrochloride, the base is recovered from 1·8 g. of the salt $B{\cdot}2HCl$, and converted to sulphate as described above for quinine base. For quinine and urea hydrochloride quinine, base is also recovered from 3 g. of the substance

$$C_{20}H_{24}O_2N_2{\cdot}HCl,CO(NH_2)_2{\cdot}HCl,5H_2O$$

and 1·5 g. of the dried recovered base neutralised as described above for quinine base. The neutral aqueous-alcoholic solutions of quinine sulphate with some sodium sulphate produced in the foregoing processes are evaporated to dryness and the powdered dry residue used for the Kerner test as described for quinine sulphate.

The pharmacopœial standards for quinine salts vary considerably, as indicated by the different amounts of ammonia solution allowed for the production of a clear solution : 6·5 c.c. in the "British Pharmacopœia" (1932), 6·0 in the "United States Pharmacopœia" (XI, 1936), 4·0 c.c. in the "German Pharmacopœia" (VI, 1926), and 4·5 c.c. in the "Dutch Pharmacopœia (V, 1926). The last-mentioned pharmacopœia accepts the Kerner test for quinine sulphate, but the general method for quinine base and salts is a polarimetric test, based on the allowed optical rotation, −17·7° to −18·0° for a di-milligram-molecule of an hydrous quinine base in a calculated equivalent of a mixture of sulphuric and hydrochloric acids, the solution being diluted to 20 c.c. with water and read in a 2 dcm. tube. Thus, in the case of quinine sulphate 782 mg., *i.e.* a molecular weight in mg. of the salt

$$(C_{20}H_{24}O_2N_2)_2{\cdot}H_2SO_4,2H_2O$$

equivalent to 746 mg. of anhydrous quinine sulphate, $(C_{20}H_{24}O_2N_2)_2{\cdot}H_2SO_4$, or to 648 mg. of anhydrous quinine base, is dissolved in water with the aid of 0·5 c.c. of 4*N*-sulphuric acid and 0·5 c.c. of 4*N*-hydrochloric acid and the solution made up to 20 c.c. and the optical rotation observed in a 2 dcm. tube. The equivalents of salt and acid used in this and some other cases are given in the following table :

Pharmacopœial substance and formula.	Equivalent wt. for 648 mg. of anhydrous base.	Acid to be added.		Optical rotation in a 2 dcm. tube.
		4*N*-HCl	4*N*-H_2SO_4	
Quinine base, $C_{20}H_{24}O_2N_2$.	—	0·5 c.c.	1 c.c.	−17·7° to −18·0° at 20°. This value must be lowered by 0·023° for each degree of temperature above 20°.
Quinine hydrochloride, $C_{20}H_{24}O_2N_2{\cdot}HCl,2H_2O$.	0·7208 g. of anhydrous salt	—	1 c.c.	
Quinine sulphate, $(C_{20}H_{24}O_2N_2)_2{\cdot}H_2SO_4,8H_2O$.	0·782 g. of salt dried at 50°–60°	0·5 c.c.	0·5 c.c.	
Quinine acid sulphate, $C_{20}H_{24}O_2N_2{\cdot}H_2SO_4,7H_2O$	0·844 g. of anhydrous salt	0·5 c.c.	—	

Hydroquinine has until recently been tested for by dissolving the quinine sulphate in dilute sulphuric acid, cooling to 0° and adding a 4% aqueous solution of potassium permanganate so long as rapid decolorisation takes place. The solution is then warmed, manganese dioxide filtered out, washed, and the filtrate and washings made alkaline and the liberated hydroquinine extracted with ether, the solvent distilled off, and the residue dried to constant weight. Processes less open to obvious objection are catalytic hydrogenation in an apparatus arranged for quantitative work, such as that described by Paget and Solomon (J.C.S. 1932, 1198) and used by Buttle, Henry and Trevan for the estimation of hydro-bases in commercial cinchona alkaloids (Biochem. J. 1934, **28**, 426) or the mercuration process of Thron and Dirscherl (Annalen, 1935, **515**, 252), which depends upon the fact that each of the four primary cinchona alkaloids, in virtue of the presence of a vinyl group in the molecule can combine with a molecule of mercuric acetate, while the hydro-bases in which the vinyl group has been reduced to an ethyl group cannot be mercurated in this fashion. The process is carried out as follows : 1 g. of the base (or an equivalent quantity of a salt) dissolved in 6 g. of 10% sulphuric acid is treated with 14 g. of a 10% solution of mercuric acetate in 5% acetic acid, and the mixture warmed for 4 hours at 40° to 50°. When cold, 10 g. of ammonia solution (sp.gr. 0·96) are added and the liberated hydro-base extracted with ether; usually 20, 10, and 10 c.c. in successive portions are sufficient. The combined ether extracts are washed with water, the solvent distilled off, and the residue of hydro-base dried at 105° and weighed. The alkaline mother-liquor is acidified with sulphuric acid, 0·5 g. of phosphorous acid added, and the solution heated to boiling for a short time. The clear liquor is then decanted from the mercury formed, the latter washed with water, and the mixed liquor and washings made alkaline with ammonia and the quinine extracted with ether.

(*c*) **Examination of Other Commercial Cinchona Alkaloids.**—Apart from quinine the only cinchona alkaloid of therapeutical importance is quinidine, of which the sulphate is included in the British and United States "Pharmacopœias." In addition to qualitative tests, *e.g.* the thalleioquin reaction, both pharmacopœias require that (*a*) 1 g. of the salt shall be soluble in 5 c.c. of a warm mixture of chloroform (2 vols.) with absolute alcohol (1 vol.), and (*b*) that when 0·5 g. of the salt in 15 c.c. of boiling distilled water is mixed with 0·5 g. of neutral potassium iodide in 5 c.c. of distilled water, the mixture being then cooled to 15° and kept at that temperature for 1 hour with frequent agitation, the filtrate on addition of 2 drops of dilute solution of ammonia does not become turbid within 1 minute.

The four primary cinchona alkaloids are divisible into a lævorotatory pair, quinine and cinchonidine, and a dextro-rotatory pair, quinidine and cinchonine. In commercial specimens the two components of each pair usually contaminate each other, but not the components of the other pair. Each of the four alkaloids is usually accompanied by its hydro base, and in cinchonine the amount of hydrocinchonine may be as much as 14% and in quinidine up to 20%.

The author has not been able to find in the literature any satisfactory systematic method for the examination of commercial samples of quinidine, cinchonine and cinchonidine, but suggests that, bearing in mind the facts quoted above, it should be easy to evolve such a method when required, *e.g.* in (1) cinchonidine, the probable impurities are (2) quinine, (3) hydroquinine, and (4) hydrocinchonidine. The vinyl bases (1) and (2) can be separated quantitatively from the hydro-bases (3) and (4) by Thron and Dirscherl's mercuration process (*see above*), and a methoxyl determination in (1)+(2), and (3)+(4) thus recovered will give the amount of quinine and hydroquinine present respectively, or the amount of each component in each mixture may be arrived at by a polarimetric estimation. The author has found it convenient in dealing with mixtures of cinchona alkaloids to determine the rotation for a $M/40$ solution of the base in $N/10$ sulphuric acid. The specific rotations for carefully purified specimens of the eight principal cinchona alkaloids under these conditions are as follows (Buttle, Henry, and Trevan, *l.c.*) :

Quinine	−284·5°
Hydroquinine . .	−235·7°
Cinchonidine . .	−178·0°
Hydrocinchonidine .	−144·6°
Quinidine . . .	+334·2°
Hydroquinidine .	+299·0°
Cinchonine . . .	+263·7°
Hydrocinchonine .	+225·8°

The figures are for anhydrous base in each case, but the equivalent of air-dry base is weighed out for the determination.

4. General Properties of the Cinchona Alkaloids.—The eight principal cinchona alkaloids above mentioned (*i.e.* cinchonine, quinine, their stereoisomerides and dihydro-derivatives) are white, odourless but intensely bitter, high-melting, crystalline solids. The bases are almost insoluble in water or aqueous solutions of salts and alkalis, but dissolve, in general, in dilute mineral acids and in a variety of organic solvents.

The four alkaloids which contain a methoxyl group (quinine, etc.), dissolved in much dilute sulphuric, nitric, or other oxy-acid, exhibit a blue fluorescence, which is particularly intense when viewed in ultra-violet light and allows of the detection of minute amounts of quinine (*see, e.g.* Canals and Peyrot, Compt. rend. 1934, **198**, 746). Solutions in the halogen hydracids are not fluorescent ; the addition of such an acid to a solution of quinine in an oxy-acid weakens, and may even destroy, its fluorescence. For a qualitative connection between the appearance of fluorescence and the chemical constitution of the alkaloids and their derivatives *see* Rabe and Marschall (Annalen, 1911, **382**, 360). A spectrographic method of determining cinchona alkaloids has been proposed by van Arkel and van der Wielen (Pharm. Weekbl. 1935, **72**, 1198; 1937, **74**, 1514).

The cinchona alkaloids respond to tests with the usual alkaloidal reagents and precipitants (*see* Alkaloids). Characteristic of the methoxylated alkaloids are the *thalleioquin* and *erythroquin* reactions. The former (Brandes, André) is carried out as follows : to an aqueous solution of, for example, a quinine salt, or to quinine dissolved in dilute acetic acid, is added a slight excess of chlorine or bromine water or a solution of bleaching powder, followed by an excess of ammonia giving rise to an emerald-green coloration or precipitate, depending on the amount of quinine present. The reaction is said to be weakened or inhibited by caffeine, antipyrine and other substances. The erythroquin reaction (Vogel, Abensour) is carried out in a similar fashion, except that before adding the ammonia, a drop of 10% potassium ferro- or ferri-cyanide is added ; the coloration produced is red : this reaction is said to be even more delicate than the thalleioquin test. The most delicate test however is that afforded by the fluorescence already mentioned.

The cinchona alkaloids are strongly optically active. They fall into two groups of four, the dextro- and lævo-rotatory series respectively. To the former belong cinchonine, quinidine, and their dihydro-derivatives ; cinchonidine, quinine, hydrocinchonidine, and hydroquinine are lævorotatory. In general, the rotations of the bases in alcohol are of the same order of magnitude as those of the neutral salts (B·HA) in water. The rotations of the salts, however, progressively increase in arithmetic value with addition of acid. A maximum is reached at about the stage at which the amount of acid added suffices to convert the neutral salt into the acid salt (B·2HA); with further additions of acid the rotation slowly falls. This characteristic behaviour was first observed by Hesse (Annalen, 1873, **166**, 217. *See also* Oudemans, *ibid.* 1876, **182**, 33 ; 1879, **197**, 48 ; 1881, **209**, 38 ; Rec. trav. chim. 1882, **1**, 18; Liquier, Compt. rend. 1926, **183**, 195; Dietzel and Söllner, Arch. Pharm. 1930, **268**, 629; Lapp, Compt. rend. 1932, **195**, 243 ; Bull. Soc. chim. 1935 [v], **2**, 1407 ; Emde, Helv. Chim. Acta, 1932, **15**, 559; Ludwiczakówna and Suszko, Bull. Acad. Polonaise, A. 1934, 402).

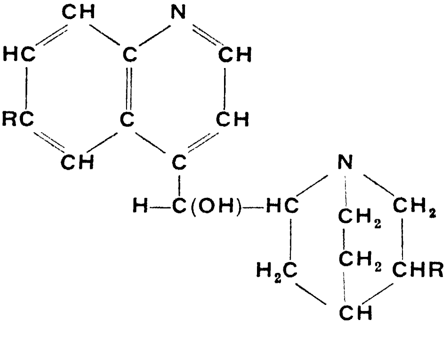
The cinchona alkaloids are strong diacidic bases, which form two series of salts, *viz.* neutral salts B·HA (called " basic " salts in France), and acid salts B·2HA (in France " neutral " salts). B·4HA is also occasionally met with. The neutral salts are neutral or faintly alkaline to litmus ; the acid salts are acid to litmus but neutral to methyl orange or Congo red. These are, in general, colourless, crystalline solids, which tend to become discoloured on exposure to light. It has been claimed that exposure of cinchona alkaloid salts in aqueous solution to direct sunlight gives rise to the cinchonatoxines (*see* p. 142), the solutions becoming in the course of time yellow or even brown in colour.

The alkaloids are not very stable. The toxines just mentioned, formed when the acid sulphates or tartrates are heated to melting, result also on so mild a treatment as boiling in dilute acetic acid solution, which, indeed, is more certain of its effect than the use of mineral acids. With more concentrated mineral acids the unsaturated alkaloids undergo complex isomerisation and transformation (*see* Section 5*d*, p. 149).

In temperate climates the cinchona alkaloids are used mainly as bitter tonics and antipyretics, but the great bulk of the quinine manufactured is used in tropical countries as a specific for the treatment of malaria. In common with the other cinchona alkaloids it exerts a direct toxic action chiefly on the asexual forms (*schizonts*) of the malarial parasite. These substances, therefore, provide an example of chemotherapeutic action, discovered and applied long before the principles upon which chemotherapeutic investigations as now conducted were laid down by Ehrlich. For over 300 years, at first in the form of cinchona bark or its galenical preparations, and in the last century as the alkaloids or their proximate derivatives, cinchona has been the sole remedy available against malaria.

As knowledge of the etiology of this disease increased it became evident that these alkaloids are not complete remedies and, in particular, it was realised that they were relatively ineffective against the sexual forms (*gametocytes*) of the malarial parasite. Within the last decade it has been found that complementary drugs exerting gametocidal action can be synthesised, of which 8-(ω-diethylamino-*iso*amyl)amino-6-methoxyquinoline (*plasmoquine*) is the best known example. This substance resulted from the joint chemical and biological investigations of Schulemann, Schönhöfer and Wingler (Klin. Woch. 1932, **11**, p. 381) with Roehl (Arch. Schiffs. Trop. Hyg. 1926, **30**, Beiheft 3, p. 11 ; 1927, **31**, Beiheft 1, p. 48). An interesting development of this work was achieved by Mietzsch and Mauss (Klin. Woch. 1933, **12**, 1276; Angew. Chem. 1934, **47**, 633), who in conjunction with Kikuth (Deut. med. Woch. 1932, **58**, 530) found that the same side-chain, inserted in position 5 in 8-chloro-3-methoxyacridine, produced the drug now known as "atebrine," which like quinine is schizonticidal in action. These successes have led to great activity in this type of investigation, not only in Germany but in this country, France, Russia and elsewhere. There are numerous other minor applications of the cinchona alkaloids in medicine, *e.g.* the use of quinine-urethane as a sclerosing agent, of quinine-urea as a local anæsthetic, and of quinidine in the treatment of auricular fibrillation. Quinine and certain of its derivatives, such as the Morgenroth compounds referred to later, are powerful bactericidal agents, and though the high expectations at first based on these results have not materialised in practice, hope has not yet been given up that it may be possible to develop practicable, pneumococcicidal agents with one or other of the cinchona alkaloids as a starting-point and work on these lines is being intensively pursued, especially in Japan and the United States.

5. Constitution of the Cinchona Alkaloids.—(*a*) **Structure.** The principal alkaloids of this group have been shown to have the following structure :



in which **R** may be hydrogen or methoxyl, and **R′** may be vinyl ($CH_2{=}CH$—) or ethyl. The eight commonest naturally occurring alkaloids comprise four structurally identical stereoisomeric pairs.

(1) Cinchonine and cinchonidine,

$C_{19}H_{22}ON_2$ (R is H—; R′ is $CH_2{=}CH$—).

(2) Hydrocinchonine and hydrocinchonidine,

$C_{19}H_{24}ON_2$ (R is H—; R′ is $CH_3{-}CH_2$—).

(3) Quinine and quinidine,

$C_{20}H_{24}O_2N_2$(R is CH_3O—; R′ is $CH_2{=}CH$—).

(4) Hydroquinine and hydroquinidine,

$C_{20}H_{26}O_2N_2$ (R is CH_3O — ; R′ is $CH_3{-}CH_2$—).

To this list may be added three other alkaloids belonging to the same chemical group. These have a phenolic character, and have not a methoxyl but a hydroxyl group in position 6 of the quinoline nucleus. Cupreine,

$C_{19}H_{22}O_2N_2$ (R = HO— ; R′ = $CH_2{=}CH$—),

was discovered in cuprea bark derived from *Remijia pedunculata* (Paul and Cownley, Pharm. J. 1881, **12**, 497 ; 1884, **15**, 221, 401 ; Hesse, Ber. 1882, **15**, 854 ; Annalen, 1884, **225**, 95), but is now unobtainable. It is the phenol corresponding to quinine, for it yields the latter on methylation (Grimaux and Arnaud, Compt. rend. 1891, **112**, 774). The other two, hydrocupreine and hydrocupreidine,

$C_{19}H_{24}O_2N_2$ (R = HO— ; R′ = $CH_3{-}CH_2$—),

are not known to occur naturally, but can be obtained by the demethylation with mineral acids of hydroquinine and hydroquinidine respectively, or, in the case of the former, by the catalytic hydrogenation of cupreine (Giemsa and Halberkann, Ber. 1918, **51** 1325). The phenol corresponding to quinidine, which would systematically receive the name cupreidine, is unknown, although Ludwiczakówna, Suszko, and Zwierzchowski (Rec. trav. chim. 1933, **52**, 847) claim to have isolated it from the products obtained by the treatment of quinidine with sulphuric acid ; their contention, however, has been convincingly refuted (Henry and Solomon, J.C.S. 1934, 1923 ; Thron and Dirscherl, Annalen 1935, **515**, 252).

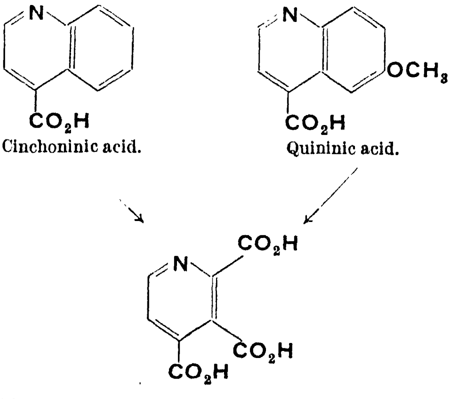
The above structural formula has not been fully elaborated for each alkaloid separately and follows mainly perhaps from work on cinchonine. The evidence for the skeletal structure of the other members of the group proceeds in part from the identity or simple mutual relation of various degradation products ; thus, for instance, cinchonine and cinchonidine give rise to identical products, however they are attacked [*e.g.* on oxidation there are formed cinchoninic acid (quinoline-4-carboxylic acid) and cincholoiponic acid (3-carboxypiperidine-4-acetic acid)] ; the same applies, on the other hand, to quinine and quinidine, except that these give rise not to cinchoninic acid itself but to its 6-methoxy derivative, quininic acid. Some evidence for the structure of certain of the alkaloids other than cinchonine arises also from the possibility of inter-conversion among them ; this, however, is very limited. Thus, all the hydro-alkaloids ($R'=CH_3-CH_2-$) are obtainable from the corresponding vinyl bases by catalytic hydrogenation. Again, cinchonidine was obtained by Koenigs and Husmann (Ber. 1896, **29**, 2185) from cinchonine by the action of amyl alcoholic potassium hydroxide, and this kind of interconversion was later extended by Rabe and his pupils (Annalen, 1932, **492**, 242) to the whole series. Finally, in evidence of the identical structure in pairs (as paired in the above list) of the cinchona alkaloids, may be mentioned the fact that each such pair gives rise to three transformation products, the identity of which is the same whichever member of the pair forms the source. These three products are, moreover, either actually isomeric with the parent alkaloids, or, at all events, have the full skeletal structure of the parent alkaloids preserved intact. They are (*see below*) the "-icines" (toxines) of Pasteur and of von Miller and Rohde, the anhydro-bases (cinchene, quinene) of Comstock and Koenigs, and the ketones (cinchoninone, quininone) of Rabe. Thus, cinchonine and cinchonidine give rise to one and the same cinchonicine (cinchotoxine) ; to one and the same cinchene, which only differs from the parent bases by the elements of water ; and to one and the same cinchoninone, differing from the parent bases by two hydrogen atoms.

The evidence for the above structural formula is in brief as follows.

Both nitrogen atoms in the molecule are tertiary and capable of salt formation. Thus not only are both neutral and acid salts known, such as $B{\cdot}HCl$, $B_2{\cdot}H_2SO_4$, and $B{\cdot}2HCl$, $B{\cdot}H_2SO_4$, but also mixed acid salts of the type $B_2{\cdot}2HCl{\cdot}H_2SO_4$ (Grimaux, Compt. rend. 1892, **115**, 608).

The alkaloids combine with one and with two molecules of an alkyl halide, forming mono- and dialkylhalides, which have the characteristic properties of quaternary ammonium salts. The nitrogen atom in the quinuclidine half of the molecule is more strongly basic than that in the quinoline half and is the one involved in neutral salt formation ; it is at the quinuclidine nitrogen atom also that the alkyl and halogen groups are added in the ordinary monoalkylhalides. Thus Claus and Weller (Ber. 1881, **14**, 1921) showed that cinchonidine ethobromide was oxidised to cinchoninic acid (quinoline-4-carboxylic acid) and not to its ethobromide. Skraup and von Norwall (Monatsh. 1894, **15**, 37) prepared a series of yellow ethiodides isomeric with the ordinary white ethiodides by treating not the free bases but the neutral hydriodides with ethyl iodide ; both forms furnished one and the same diethiodide when treated with a further molecule of ethyl iodide. Skraup later (*ibid.* p. 433) oxidised the yellow form of cinchonine ethiodide and obtained the ethiodide of cinchoninic acid, thus showing that in cinchonine hydriodide it is the quinuclidine basic centre which is satisfied. Similarly, Claus and Mallmann (Ber. 1881, **14**, 76) found that the treatment of quinine methiodide with ethyl iodide gave rise to a different product from that obtained by the action of methyl iodide on quinine ethiodide. The two "ethmethiodides" were isomeric (*cf.* Claus, Annalen, 1892, **269**, 232 ; and Konek, Chem. Zentr. 1936, ii, 1352 ; 1937, i, 1694 ; 1938, i, 75).

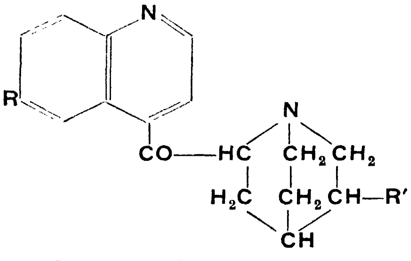
That one of the two oxygen atoms in quinine and quinidine is a member of a methoxyl group follows partly from the fact that these alkaloids can be demethylated (*e.g.* by heating with hydrochloric acid) ; there are then formed phenolic bases and methyl chloride (*see, e.g.*, Hesse, Annalen, 1880, **205**, 314). The other evidence for the presence of a methoxyl group, evidence, moreover, which serves to indicate the position of this group in the molecule, arises from the fact that in those degradation experiments (such as oxidation) in which cinchonine and cinchonidine give rise to simple quinoline derivatives (such as cinchoninic acid), quinine and quinidine furnish the corresponding 6-methoxyquinoline derivatives. Thus Skraup (Monatsh. 1881, **2**, 587) found that quinine on oxidation with chromic acid gave rise to quininic acid (6-methoxyquinolinecarboxylic acid), and that this, on more vigorous oxidation with the same reagent, was degraded to the same pyridinetricarboxylic acid which could be obtained in like manner from cinchoninic acid, the oxidation product of cinchonine :



Cinchoninic acid. Quininic acid.

The constitution of the latter acid being known (*see* Skraup, Annalen, 1880, **201**, 291), it followed that the methoxyl group in quininic acid was contained in the benzene and not in the pyridine nucleus. He further showed (Monatsh. 1883, **4**, 695) that quininic acid could be demethylated by means of hydrochloric acid to the corresponding phenolic acid, to which he gave the name xanthoquininic acid, and that this, on decarboxylation, gave rise to the known 6-(or *p*-)hydroxyquinoline. There is, therefore, in quininic acid (as well as in quinine and quinidine) a methoxyl group in the 6-position of the quinoline nucleus, which is absent in the cases of cinchoninic acid, cinchonine, and cinchonidine.

The second oxygen atom in quinine and quinidine, or the sole oxygen atom in cinchonine and cinchonidine, belongs to a hydroxyl group. This was first shown by Schützenberger (Compt. rend. 1858, **47**, 233), who prepared the acetyl and benzoyl derivatives of cinchonine and of quinine. Hesse (Annalen, 1880, **205**, 314) has prepared the acetyl derivatives of all the four alkaloids. The demonstration, however, only acquires strict cogency when taken in conjunction with the later proof that these bases are ditertiary (*see above*). Independent of this proof, however, is the evidence adduced by Koenigs (Ber. 1880, **13**, 285), who treated cinchonine hydrochloride with a mixture of phosphorus penta- and oxy- chloride and obtained a product, $C_{19}H_{21}NCl$, cinchonine chloride, in which the hydroxyl group had been replaced by chlorine. The nature of the hydroxyl group was elucidated by Rabe and his collaborators (Ber. 1907, **40**, 3655; 1908, **41**, 62, 872; Annalen, 1909, **364**, 330), who made the discovery that on very gentle oxidation with chromic acid cinchonine lost two hydrogen atoms and was converted into the corresponding ketone, cinchoninone, being otherwise unchanged. Cinchoninone formed an oxime, and cinchonine could be recovered again from its reduction products:



Cinchoninone (R = H; R′ = vinyl).

The cinchona alkaloids, therefore, contain a secondary alcoholic grouping, $-CH(OH)-$; its position in the molecule will be made clear in the sequel.

The existence of an unsaturated side-chain (*i.e.* of the vinyl group) in cinchonine, quinine, and their stereoisomerides is revealed by their behaviour with the halogens, the halogen hydracids, and with potassium permanganate. Laurent (Compt. rend. 1845, **20**, 1587; Ann. Chim. 1848, (iii), **24**, 302) first studied the action of chlorine and bromine on cinchonine. Direct addition of two atoms of the halogen occurs, cinchonine dichloride and dibromide being formed. Comstock and Koenigs (Ber. 1884, **17**, 995; 1886, **19**, 2853; 1892, **25**, 1539) have also prepared these dihalogen addition compounds, as well as quinine dibromide, and made a detailed study of them. On treatment with alcoholic potash the dibromides lose two molecules of hydrogen bromide, dehydrocinchonine, $C_{19}H_{20}ON_2$, and dehydroquinine, $C_{20}H_{22}O_2N_2$, being formed. These latter substances contain an acetylenic linkage in place of the double bond of the parent bases ($R'=CH\equiv C-$) (Koenigs, Ber. 1895, **28**, 1986). With the halogen hydracids, also, simple addition takes place, the side-chain R′ presumably becoming CH_3—$CH(Hal)$—. This cannot, however, as yet be considered as having been quite firmly established.

Zorn (J. pr. Chem. 1873, **8**, 279), influenced by the contemporary researches of Matthiessen and Wright on narcotine and other opium alkaloids, was first led to study the action of strong hydrochloric acid on cinchonine and quinine (*see also* Hesse, Annalen, 1874, **174**, 340; 1880, **205**, 314). Skraup (Annalen, 1880, **201**, 324) first treated cinchonine with hydrobromic acid, and Lippmann and Fleissner (Monatsh. 1891, **12**, 327) heated quinine with hydriodic acid. In all these cases substances of the general type HBHal,2HHal (where B stands for the original vinyl alkaloid) were formed, except that the methoxylated alkaloids (*e.g.* quinine) were simultaneously demethylated. Comstock and Koenigs (Ber. 1887, **20**, 2510) showed that the reaction proceeded not only on heating but also at room temperature, and obtained in this way not only the ordinary chloro- and bromohydrocinchonine but also chloro- and bromohydroquinine, which still contain the methoxyl group. A copious literature has accumulated dealing with this reaction.

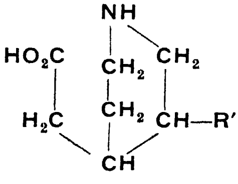
The formation of halogen derivatives, whether by the addition of the free elements or by treatment with the hydracids, indicates only the presence in the molecule of an unsaturated centre. The existence of a side-chain, and the fact that the double bond is contained therein, is shown by the behaviour of the vinyl-alkaloids with potassium permanganate. Whereas the hydro-alkaloids react but slowly or not at all (it is this property which led to their discovery and isolation), the unsaturated alkaloids instantly decolourise a dilute, ice-cold, acid solution of this reagent. Kerner first studied the behaviour of quinine (Zeit. f. Chemie, 1869, **5**, 593) and found that formic acid was produced together with a substance which he called quitenine, $C_{19}H_{22}O_4N_2$ (*see also* Skraup, Annalen, 1879, **199**, 348). Similarly, Willm and Caventou (Annalen, 1870, Suppl. VII, 249), Hesse (Annalen, 1875, **176**, 232), and Skraup (*ibid.* 1879, **197**, 376) obtained cinchotenine, $C_{18}H_{20}O_3N_2$, from cinchonine, Skraup and Vortmann (*ibid.* p. 235) obtained cinchotenidine from cinchonidine, and Forst and Boehringer (Ber. 1882, **15**, 1659) oxidised quinidine to quitenidine. These "tenines" result by the loss of one carbon atom as formic acid; they are, unlike the parent alkaloids, saturated substances which, for example, do not react with hydriodic acid; they are tertiary bases and still contain a hydroxyl group; and finally they are carboxylic acids which form salts and esters. These results were summarised by Skraup (Ber. 1895, **28**, 12), who justifiably drew the conclusion that the unsaturated cinchona alkaloids contain a vinyl group, and that the "tenines" are the otherwise unchanged carboxylic acids ($R' = -COOH$).

Evidence to the same effect has been obtained by Seekles (Rec. trav. chim. 1923, **42**, 69); under the influence of ozone the cinchona alkaloids form ozonides, which on hydrolysis give rise to aldehydes ($R' = -CHO$), corresponding to the "tenines." Seekles gave these the termination -al; thus cinchoninal, $C_{18}H_{20}O_2N_2$, and quininal, $C_{19}H_{22}O_3N_2$. The position of the vinyl (or ethyl) group in the molecule will appear in the subsequent discussion.

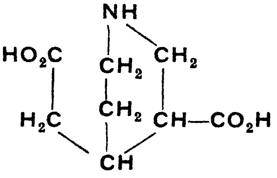
The skeleton of the molecule of the cinchona alkaloids naturally and historically falls into two portions or "halves": the quinoline portion or the "first half," and the remainder of the molecule or the "second half." The molecule readily undergoes fission in a corresponding manner, there being formed on the one hand simple derivatives of quinoline or 6-methoxyquinoline, and, on the other hand, more complex derivatives of piperidine. The structure of the skeleton, and at the same time the position of the hydroxyl and vinyl (or ethyl) groups, was deduced from a study of such degradation products.

There are, broadly, three ways in which such a fission can be effected.

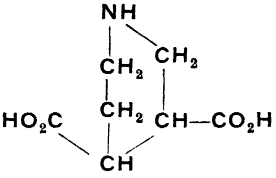
The first method, due mainly to Skraup, is by oxidation with chromic acid, when the "first half" gives rise to the quinolinecarboxylic acids already mentioned, viz. cinchoninic and quininic acids. They are sparingly soluble readily isolable substances, and it is in their filtrates and mother-liquors (which when simply evaporated afford intractable syrups) that the following substances derived from the "second half" are found: meroquinene (from the vinyl-alkaloids), cincholoipon (from the hydro-alkaloids), and the oxidation products of these, cincholoiponic and loiponic acids (Skraup, Monatsh. 1888, **9**, 783; 1896, **17**, 365; Koenigs, Ber. 1894, **27**, 1501).



Meroquinene (R' is $CH_2{=}CH-$)
Cincholoipon (R' is CH_3-CH_2-).



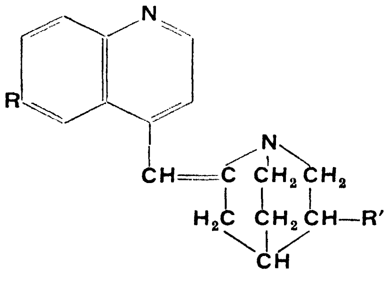
Cincholoiponic acid.



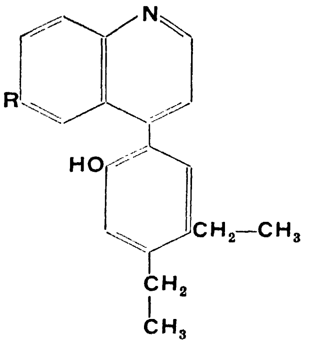
Loiponic acid.

Exactly the same substances result from the oxidation of the three sets of transformation products referred to above, *viz.* from the "toxines" (Skraup and Würstl, Monatsh. 1889, **10**, 220), the anhydro-bases (Comstock and Koenigs, Ber. 1884, **17**, 1990), and from Rabe's ketones (Ber. 1907, **40**, 3657), thus showing the close relationship of these substances to the parent alkaloids. The same applies also to the saturated carboxylic acids, the "tenines" (formed by oxidation of the parent vinyl alkaloids with potassium permanganate), except that in this case neither meroquinene nor cincholoipon are formed, but only the quinolinecarboxylic acids, and cincholoiponic and loiponic acids (Skraup, Monatsh. 1889, **10**, 42).

The second method of fission was discovered by Koenigs. When the hydrochlorides of the cinchona alkaloids in chloroform suspension are treated with phosphorus pentachloride there are formed, as already mentioned, substances such as cinchonine chloride and quinine chloride, in which the original hydroxyl group is replaced by chlorine (Comstock and Koenigs, Ber. 1884, **17**, 1984; 1885, **18**, 1219). For the corresponding bromides, *see* C. F. Boehringer und Soehne, G.m.b.H., Rabe, Cohaupe, and Scheel, G.P. 592540 and 592541, 1934). These chlorides, on treatment with alcoholic potash, lose a molecule of hydrogen chloride with the production of a double bond. The "anhydro-bases" so formed are known as quinene, cinchene, hydroquinene (Giemsa and Halberkann, Ber. 1921, **54**, [B], 1194) and hydrocinchene, each being the identical product from two stereoisomeric parent alkaloids; thus both quinine chloride and quinidine chloride give rise to one and the same quinene.



Quinene (R is CH_3O-; R' is $CH_2{=}CH-$).
Cinchene (R is $H-$; R' is $CH_2{=}CH-$).
Hydroquinene (R is CH_3O-; R' is CH_3-CH_2-).
Hydrocinchene (R is $H-$; R' is CH_3-CH_2-).



*apo*Cinchene (R is H—).
*apo*Quinene (R is HO—).

When heated with hydrobromic acid, the anhydro-bases undergo an extraordinary reaction (Comstock and Koenigs, Ber. 1881, **14**, 1854; 1885, **18**, 1226, 2379; 1887, **20**, 2674). The so-called *apo*cinchene and *apo*quinene formed were found to be derivatives of phenylquinoline having the structure shown (*see* Koenigs, Ber. 1894, **27**, 900; J. pr. Chem. 1900, **61**, 1; Kenner and Statham, J.C.S. 1935, 299; and Kenner and Nandi, Ber. 1936, **69**, 635). The vinyl group seems to be essential in the mechanism of this transformation, for, hydrocinchene does not react with hydrobromic acid (Koenigs, Ber. 1894, **27**, 1504), and hydroquinene with hydrochloric acid only undergoes demethylation (Giemsa and Halberkann, Ber. 1921, **54**, 1195). This is suggestive in connection with the behaviour of the cinchona alkaloids with mineral acids (*see below*).

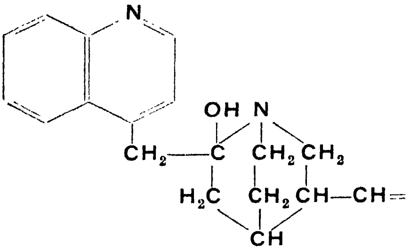
The reaction, however, does not throw much light on the constitution of the alkaloids. Much more illuminating is the treatment of the anhydro-bases with phosphoric acid at 170° (Koenigs, Ber. 1894, **27**, 900), which constitutes the second method of fission of the cinchona alkaloids. Hydrolysis occurs, 2 molecules of water being taken up, and there are formed lepidine (4-methyl-quinoline) from cinchene, and its 6-methoxy-derivative from quinene. The former substance, derived from the "first half," is also formed from hydrocinchene (Koenigs and Hoerlin, Ber. 1894, **27** 2290). The "second half" gives rise to the same substances which are formed in Skraup's chromic acid oxidation, viz. meroquinene from cinchene and quinene, and cincholoipon from hydrocinchene. The oxidation products of these, cincholoiponic and loiponic acid, are not formed in this reaction.

Before proceeding to the third method of fission, and to the remainder of the evidence for the structural formula set out above, it will be convenient first to deal with the constitution of the degradation products already mentioned, and to summarise the conclusions which can be drawn.

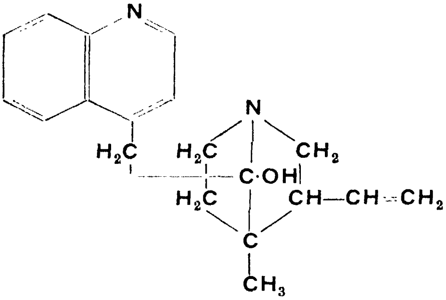
A full discussion of the nature of these substances, however, would go far beyond the scope of this article. It will suffice, in the case of the quinoline derivatives (from the "first half") to mention, as a matter of historical interest, that the presence of a quinoline nucleus was early recognised, for Gerhardt (1843) had obtained quinoline itself (then unknown) by the distillation of cinchonine with potash, and it was incidental to the investigation of these alkaloids that the constitution of this important heterocyclic base was studied. It was synthesised almost simultaneously in 1879 by Koenigs, by Skraup, and by Baeyer.

In regard to the degradation products derived from the "second half," meroquinene, cincholoipon, cincholoiponic acid, and loiponic acid, it must suffice to append a bibliography of papers by Skraup and by Koenigs, who, almost exclusively, studied and elucidated the constitution of these substances. [Skraup's papers are to be found in Monatsch., 1888, **9**, 783; 1895, **16**, 159; 1896, **17**, 365; 1900, **21**, 879; (with Piccoli), *ibid.* 1902, **23**, 269. The relevant papers by Koenigs are in Ber., 1894, **27**, 900, 1501; 1895, **28**, 1896, 3150; 1897, **30**, 1326; 1902, **35**, 1349; 1904, **37**, 3244; (with Bernhart), *ibid.* 1905, **38**, 3049. For a very full account of the chemistry of meroquinene, *see* the experimental portion of Koenigs' "chef d'œuvre" (Annalen, 1906, **347**, 193); the theoretical portion of this paper (p. 143 *et seq.*) is entirely devoted to a full and valuable review of the then existing knowledge of the constitution of the cinchona alkaloids. For a synthesis of cincholoiponic acid, *see* Wohl and Losanitsch (Ber. 1907, **40**, 4698; Wohl and Maag, *ibid.*, 1909, **42**, 627).]

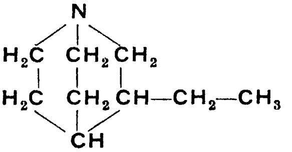
The molecules of cinchoninic acid ("first half") and of meroquinene ("second half") account between them for all the 19 carbon atoms of cinchonine; further, the constitution of meroquinene fixes the vinyl group in a 3-position to the piperidine nitrogen atom; of the three such possible positions, two are structurally identical, being only stereochemically distinct, while the third, made improbable by the manner of formation of meroquinene by Skraup's method of oxidation, is impossible in the light of its formation by the hydrolytic process of Koenigs. Finally, seeing that the nitrogen atom in the "second half" of the cinchonine molecule is tertiary, while that of meroquinene is secondary, and because no further carbon atoms (such as a *N*-methyl group) can be accommodated, it follows that either the acetic acid residue in the 4-position of meroquinene or the carbon atom of the carboxyl group of cinchoninic acid, must, in some way, be joined to the nitrogen atom in the cinchonine molecule. Of the several possibilities which these considerations open for the structural formula of cinchonine, I and II (p. 142) were envisaged by von Miller and Rohde (Ber. 1895, **28**, 1059); II which was originally preferred, was later rejected in favour of I by Koenigs (J. pr. Chem. 1900, [ii], **61**, 11): he proposed the name "quinuclidine" for the parent structure, from which the "second half" of the following formula is derived hypothetically, and succeeded in preparing two stereoisomeric 3-ethylquinuclidines, one from meroquinene, and the other, by a different method, from cincholoipon (Ber. 1904, **37**, 3244). The formula accepted at the present time, which is set forth at the beginning of this section, was first considered by Rabe and Ritter (Annalen, 1906,



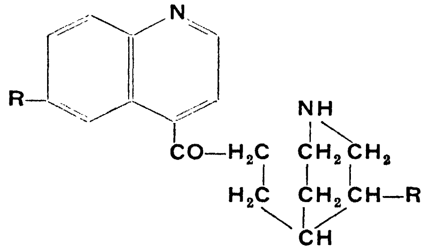
Cinchonine (von Miller and Rohde, 1895, I; Koenigs, 1900).



Cinchonine (von Miller and Rohde, 1895, II)



3-Ethylquinuclidine (Koenigs, 1904).



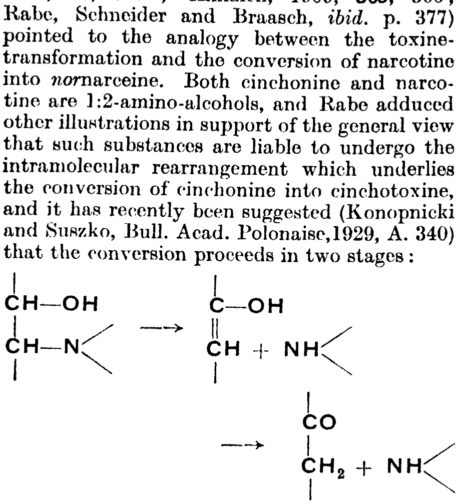
Cinchonatoxines.

350, 180); it was adopted by Koenigs, Bernhart, and Ibele (Ber. 1907, **40**, 648, 2873), by Rohde and Antonaz (*ibid.* 1907, **40**, 2329), and finally singled out by a process of elimination by Rabe, Kuliga, and Naumann (Annalen, 1909, **365**, 353). And it is this work of Rabe's which must now bring us back to the consideration of the third method available for the degradation of the cinchona alkaloids.

In 1853 Pasteur (Compt. rend. 1853, **37**, 110) discovered that the acid sulphates of the cinchona alkaloids melt when heated with a little water at 140° and give rise to isomerides. Thus from cinchonine he obtained a substance which he called cinchonicine, and from quinine quinicine. Moreover, cinchonidine gave rise to the same cinchonicine which was also formed from cinchonine. Similarly quinicine was obtained not only from quinine but also from quinidine. These substances, which are now, for reasons to be stated below, perhaps best described as the cinchonatoxines, or briefly as the *toxines*, have the constitution shown above.

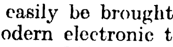
The study of the toxines has played an essential part in the investigation of the parent alkaloids, but the manner of arriving at the constitution of the former, which can hardly be dealt with apart from a description of the researches which led to the formula of the latter will not be indicated in detail. Nevertheless, some salient points of interest may be mentioned.

Two other methods exist whereby the cinchona alkaloids can be converted into the isomeric toxines. One of these was unwittingly discovered by Claus and his pupils in 1878, and the other was developed by von Miller and Rohde in 1894 while engaged on a study of the Claus reaction. The former chemist (Ber. 1878, **11**, 1820) found that the quaternary addition compounds of the cinchona alkaloids with one molecule of an alkyl halide, when boiled with potassium hydroxide in aqueous solution, reverted to tertiary bases. He regarded these as ordinary homologues of the parent alkaloids; many substances of the general type " methylcinchonine " were described in several papers (*see*, for instance, Claus and Müller, Ber. 1880, **13**, 2290; Claus and Mallmann, *ibid.* 1881, **14**, 76; Claus, Annalen, 1892, **269**, 232). von Miller and Rohde (Ber. 1894, **27**, 1187) found that these " homologues " formed phenylhydrazones, and could not therefore have the parent structure. The parent alkaloids were not attacked by the reagent used (a solution of phenylhydrazine in acetic acid) unless heated with it at 100° for a long time. It was then found (*ibid.* p. 1279) that cinchonine on heating with dilute acetic acid at 105° for 24 hours was transformed into a ketonic base, which reacted with phenylhydrazine at once, and which, on methylation with methyl iodide and sodium hydroxide, afforded a *N*-methyl derivative identical with Claus's " methylcinchonine." The ketonic base, on account of its alleged poisonous properties and loss of antipyretic action, was given the name " cinchotoxine " (*ibid.* 1895, **28**, 1058). Its identity with Pasteur's cinchonicine was also suggested. Apart from their physiological properties, the toxines were found to be remarkable in several other ways. As Pasteur had already noted, they had a greatly diminished optical rotatory power, and the toxines from stereoisomeric pairs of parent alkaloids of opposite sign of rotation were identical; the alkaloids had become converted into ketones and secondary bases; finally, the rupture of the C—N linkage was remarkable in taking place more readily with weak organic acids (acetic, tartaric, phosphoric) than with strong mineral acids such as hydrochloric acid (Rabe and McMillan, Ber. 1910, **43**, 3308; Rabe, *ibid.* 1912, **45**, 2927). Biddle (*ibid.* 1912, **45**, 526, 2832) independently made the same observation concerning the cause of this reaction, and in the course of detailed physico-chemical researches with several pupils (J. Amer. Chem. Soc. 1913, **35**, 418; 1915, **37**, 2065, 2082, 2088; 1916, **38**, 901; 1917, **39**, 968) reached the conclusion that it was catalysed neither by hydrogen ions, nor by the anions of acids, but by undissociated molecules of acids, a sufficient concentration of which was only attainable in the case of weak organic acids. Rabe (Ber. 1907, **40**, 3282; Annalen, 1909, **365**, 366; Rabe, Schneider and Braasch, *ibid.* p. 377) pointed to the analogy between the toxine-transformation and the conversion of narcotine into *nor*narceine. Both cinchonine and narcotine are 1:2-amino-alcohols, and Rabe adduced other illustrations in support of the general view that such substances are liable to undergo the intramolecular rearrangement which underlies the conversion of cinchonine into cinchotoxine, and it has recently been suggested (Konopnicki and Suszko, Bull. Acad. Polonaise, 1929, A. 340) that the conversion proceeds in two stages:



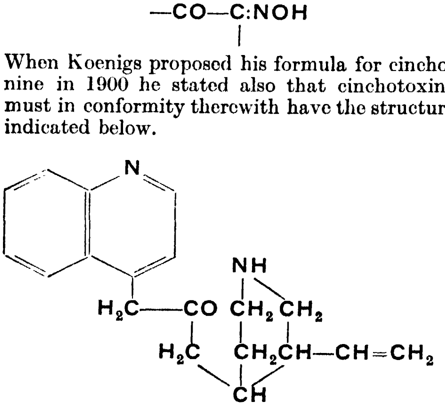
Substances of the intermediate enolic stage, in which the enolic group is fixed by intramolecular participation in an ether function, have been isolated, and it is proposed that the von Miller and Rohde toxine- nomenclature be reserved for the final ketonic substances, while Pasteur's original " -icine "- nomenclature be adopted for the new enol-ethers. The toxine transformation can easily be brought into excellent accord with modern electronic theory (*see*, for instance, Hanhart and Ingold, J.C.S. 1927, 997).

The toxines react with hydroxylamine to form ketoximes and condense with one molecule of amyl nitrite in the presence of sodium ethoxide giving rise to *iso*nitrosoketones of the type



$$\text{—CO—}\underset{|}{\text{C}}\text{:NOH}$$

When Koenigs proposed his formula for cinchonine in 1900 he stated also that cinchotoxine must in conformity therewith have the structure indicated below.

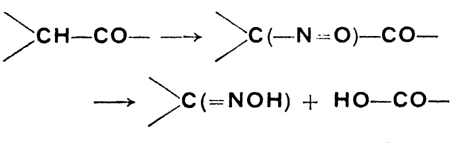


Cinchotoxine (Koenigs, 1900).

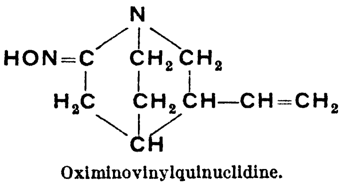
Such a substance should react with two molecules of amyl nitrite to form a di*iso*nitrosoketone of the type

$$\text{HON:}\overset{|}{\text{C}}\text{—CO—}\overset{|}{\text{C}}\text{:NOH}$$

von Miller, Rohde, Brunner and Fussenegger (Ber. 1900, **33**, 3214) failed to make cinchotoxine react with more than one molecule of amyl nitrite. The final disproof of Koenigs' formula, and support for the formula proposed by Rabe, came on the one hand from Koenigs himself and on the other from Rabe. In each case oximino- or *iso*nitrosotoxines were shown to undergo smooth rupture, into simple quinoline derivatives, from the "first half," and piperidine derivatives from the second, when subjected to the Beckmann rearrangement. Thus, Koenigs, Bernhart and Ibele (Ber. 1907, **40**, 648, 2873) treated the oxime of *N*-methylcinchotoxine with phosphorus pentachloride, and hydrolysed the product with aqueous-methyl alcoholic sodium hydroxide, or with dilute hydrochloric acid. There were formed 4-aminoquinoline, cinchoninic acid, *N*-methylmeroquinene and (probably) β-4-(*N*-methyl-3-vinylpiperidyl)-ethylamine, products which were decisive for Rabe's formula as against that of Koenigs. Again, Rabe (with Ritter, Ber. 1905, **38**, 2770; with Ackermann, *ibid.* 1907, **40**, 2013) subjected *iso*nitroso-*N*-methylcinchotoxine and *iso*nitroso-*N*-methylhydrocinchotoxine to the Beckmann rearrangement, and obtained cinchoninic acid and, from the first, the readily isolable nitrile of *N*-methylmeroquinene, from the second, the corresponding cincholoipon derivative. At about this time, also, as has already been mentioned, Rabe suceeded in oxidising the secondary hydroxylic cinchona alkaloids to the corresponding ketones, in itself decisive evidence for his secondary hydroxylic formula as against Koenigs' tertiary one. As he pointed out, however, other formulæ, also containing a secondary hydroxyl group, were conceivable, and these were finally disposed of by studying the action of amyl nitrite on the ketones (Rabe, Ber. 1908, **41**, 62; Rabe, Kuliga and Naumann, Annalen, 1909, **365**, 353). The alternative formulæ envisaged by Rabe contain a $\text{—CH}_2\text{—CO—}$ group, and demand the formation of *iso*nitrosoketones. Instead, it was found that fission once again took place in accordance with the scheme



There were formed, that is to say, cinchoninic acid and oximinovinylquinuclidine.



Oximinovinylquinuclidine.

Quininone, similarly, gave rise to this oximino-substance and to quininic acid, and hydrocinchoninine furnished cinchoninic acid and oximinoethylquinuclidine. The oximino- substances on hydrolysis, afforded hydroxylamine, with meroquinene from the one and cincholoipon from the other.

The constitution of the cinchona alkaloids as well as of the cinchonatoxines had, in this way, been finally established.

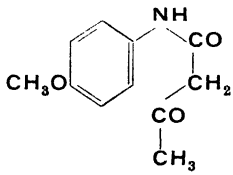
(*b*) **Synthesis.**—This constitution was verified in 1931 by the synthesis of hydroquinine and hydroquinidine (Rabe, Huntenburg, Schultze and Volger, Ber. 1931, **64**, 2487). The synthesis is in four phases:

Synthesis of quininic acid.
Synthesis of *homo*cincholoipon (VI).
Condensation of quininic acid with *homo*cincholoipon to form hydroquinotoxine.
Conversion of hydroquinotoxine to hydroquinine and hydroquinidine.

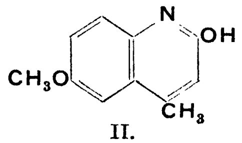
Synthesis of Quininic Acid.—The first phase, which constitutes a modification of Knorr's quinoline synthesis (Annalen, 1886, **236**, 69), proceeds in six stages:

1. Acetoacetic ester is condensed with *p*-anisidine by heating the components together.

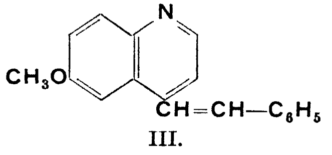
2. The resulting *p*-methoxyacetoacetanilide (I) is ring-closed by means of 90% sulphuric acid to 2-hydroxy-6-methoxy-4-methylquinoline (II).



I.



II.



III.

3. This is converted to the corresponding chloromethoxymethylquinoline by treatment with a mixture of phosphorus oxy- and pentachloride.

4. The chlorine atom is then eliminated by reduction either catalytially in alkaline alcoholic solution, or by means of aluminium and acetic acid. There is then formed *p*-methoxylepidine (6-methoxy-4-methylquinoline).

The direct oxidation of 6-methoxylepidine does not proceed smoothly, and it was found better—

5. To condense it with benzaldehyde in the presence of zinc chloride to the corresponding C-benzylidene compound (III), and then finally—

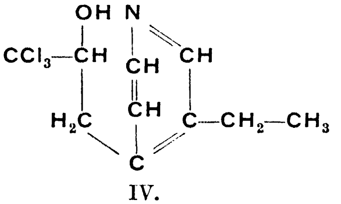
6. To oxidise this styrylquinoline derivative with cold potassium permanganate in aqueous pyridine solution to 6-methoxyquinoline-4-carboxylic acid (quininic acid) ; *cf.* Kaufmann and Peyer, Ber. 1912, **45**, 1805.

Synthesis of homo*Cincholoipon.*—The second phase, the synthesis of *homo*cincholoipon, proceeds in three stages. The method used had been worked out for a lower homologue by Rabe and Kindler (Ber. 1919, **52**, 1846). The starting material, *β*-collidine, or 4-methyl-3-ethylpyridine, which was discovered by Greville Williams (1855) and Oechsner de Coninck (Compt. rend. 1880, **91**, 296; Ann. Chim. 1882, [v], **27**, 469) in the products of distillation of cinchonine with potash, had been synthesised by Ruzicka and Fornasir (Helv. Chim. Acta, 1919, **2**, 338 ; *see also* Rabe and Jantzen, Ber. 1921, **54**, 925; E. Königs and Ottmann, *ibid.* p. 1343).

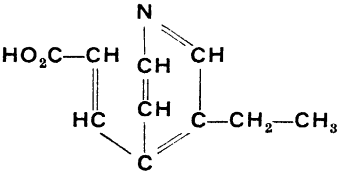
1. *β*-Collidine at 85° is condensed by means of zinc chloride with chloral.

2. The resulting compound (IV) is converted by means of alcoholic sodium ethoxide into the acrylic acid derivative V, which is then—

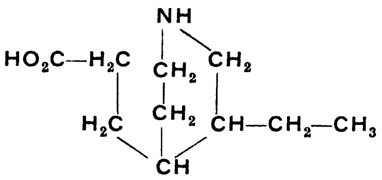
3. Catalytically hydrogenated in hydrochloric acid solution to give *homo*cincholoipon (VI).



IV.



V.

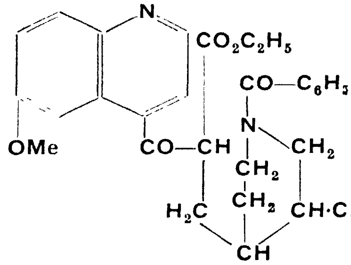


VI.

The last stage results in a mixture of stereoisomerides of which *homo*cincholoipon is one; it can be isolated by fractional crystallisation of the *d*-tartrates of their ethyl esters. The desired stereoisomeride is obtained in preponderating proportion only by rigidly adhering to a set of narrowly prescribed conditions in carrying out the hydrogenation. Among these may be mentioned the recommendation that the platinum catalyst be specially activated by the method of Vavon (Ann. Chim. 1914, [ix], 1,

149) and that the reduction be carried out at a pressure of 3 atmospheres and at 60°–70°.

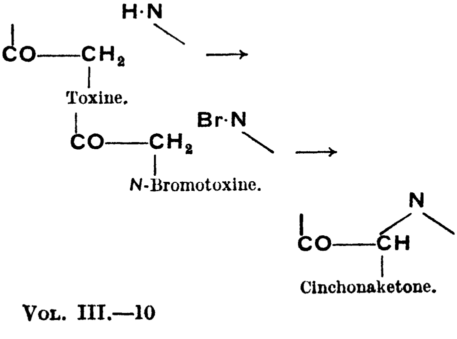
Condensation of Quininic Acid with homo-Cincholoipon.—In the next phase of the synthesis quininic ester is condensed with *homo*cincholoipon ester—the latter in the form of its *N*-benzoyl derivative—by the Claisen method. Rabe and Kindler (Ber. 1918, **51**, 1360) had already, thirteen years earlier, succeeded in condensing cinchoninic ester with non-synthetic *homo*cincholoipon to form hydrocinchotoxine, and had obtained hydroquinotoxine from quininic ester in like manner (*ibid.* 1919, **52**, 1842). The latter condensation, under the agency of sodium ethoxide and in the absence of a solvent, was now repeated with synthetic *N*-benzoyl*homo*cincholoipon ethyl ester. The product (VII) was hydrolysed by means of hydrochloric acid, the carbethoxy and benzoyl groups being removed, and hydroquinotoxine formed.



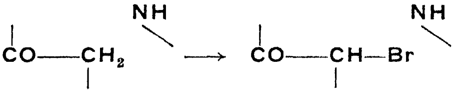
VII.

Conversion of Hydroquinotoxine to Hydroquinine and Hydroquinidine.—The conversion of hydroquinotoxine to hydroquinine and hydroquinidine in the last phase of the synthesis, which proceeds in three stages, is the earliest phase to have been elaborated, and dates back to 1908. In the first two stages hydroquinotoxine is converted to hydroquininone, and this is then reduced.

Two methods exist for the conversion of cinchonatoxines to cinchonaketones. One was first described by Rabe in the case of cinchotoxine (Ber. 1911, **44**, 2088). The other was devised by Kaufmann and Huber (Ber. 1913, **46**, 2913) for hydrocinchotoxine and hydroquinotoxine. According to Rabe's method the toxine is brominated by means of hypobromous acid to a *N*-bromotoxine, which then, under the agency of sodium ethoxide in alcoholic solution, undergoes intramolecular alkylation: hydrogen bromide is eliminated, the quinuclidine ring is closed, and a cinchonaketone formed:



Kaufmann's method is similar. By brominating with a mixture of bromine and strong hydrobromic acid a **C**-bromotoxine is formed:



The second stage is identical with Rabe's, a cinchonaketone being produced also in this case by an analogous mechanism.

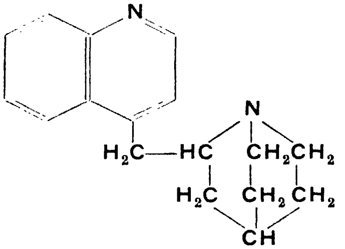
Each method has certain advantages over the other. While Rabe's procedure is applicable to both saturated and unsaturated toxines, Kaufmann's reaction is unsuitable for the latter. Rabe's method, moreover, can be effected in one operation by the use of sodium hypobromite. On the other hand, the **C**-bromotoxines lend themselves to manipulation more readily than do the **N**-bromotoxines; they separate in the course of the bromination as finely crystalline dihydrobromides. For the complete synthesis in 1931, Rabe and his collaborators actually used Kaufmann's method.

The last stage, the reduction of hydroquininone to hydroquinine and hydroquinidine (for a discussion of the formation of both alkaloids from the one ketone, *see* next section (*c*)), was the first to be achieved, for Rabe, already in 1908, had obtained cinchonine by reducing cinchoninone with sodium in alcoholic solution, and with iron filings in acetic acid (Ber. 1908, **41**, 67). Kaufmann and Huber (*l.c.*) reduced hydrocinchoninone with palladium black and hydrogen and were the first to obtain *two* stereoisomeric carbinols: hydrocinchonine and hydrocinchonidine. The other hydro-alkaloids were prepared from non-synthetic sources in a similar manner (Rabe, Z. angew. Chem. 1913, **26** 543). The vinyl alkaloids proved more difficult to prepare from the ketones, because the vinyl group on catalytic hydrogenation was also reduced. A reducing agent suitable for this purpose, which would attack the ketone group but leave the vinyl group and the quinoline nucleus intact, was finally found in aluminium metal, used on an alcoholic solution of the ketone in the presence of sodium ethoxide (Rabe and Kindler, Ber. 1918, **51**, 466; Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H., G.P. 330813, 1920).

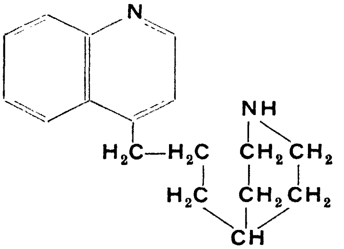
In the synthesis described in 1931, with which we are here concerned, the synthetic hydroquininone was reduced by means of hydrogen and palladium black. A freshly prepared solution of the crystalline ketone, which contains a preponderant proportion of one of the two tautomeric forms [*see* section (*c*)], gave largely hydroquinidine which was isolated as the tartrate. A little of a new stereoisomeride (m.p. 121°; $[\alpha]_D$ +70·9°) was also obtained. Hydroquinine was obtained by the reduction of an oily equilibrium mixture of tautomeric forms.

Although a complete synthesis of hydrocinchonine and hydrocinchonidine has not been formally described, these substances can virtually be considered to have been synthesised. They have been obtained from hydrocinchoninone, and this from hydrocinchotoxine (Kaufmann and Huber, *l.c.*). Hydrocinchotoxine has been prepared from cinchoninic ester and **N**-benzoyl-*homo*cincholoipon ester (Rabe and Kindler, Ber. 1918, **51**, 1360). The latter substance had at that time only been obtained by the oxidation of **N**-benzoylhydrocinchotoxine (Kaufmann and Brunnschweiler, Ber. 1916, **49**, 2302), but has now, as we have seen, been synthesised. Finally, cinchoninic acid was synthesised by Pfitzinger (J. pr. Chem. 1902, [ii], **66**, 263 ; *cf.* Thielepape, Ber. 1938, **71**, 387.) The case is different for the unsaturated alkaloids cinchonine and quinine, the syntheses of which present peculiar difficulties.

It is of interest to note here, that by an analogous series of reactions substances have been prepared from which the cinchona alkaloids may be considered to be derived. In 1922 Rabe (Ber. 1922, **55**, [B], 522) proposed the names "rubane" and "rubatoxane" for the following structures :



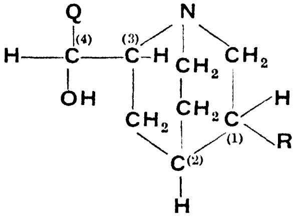
Rubane.



Rubatoxane.

Rubatoxanone and rubanone, the analogues of the cinchonatoxines and cinchonaketones respectively, were described by Rabe, Kindler, and Wagner (Ber. 1922, **55**, [B], 532); rubane itself (in optically active *d*- and *l*- forms), the four rubanols (the analogues of the cinchona alkaloids), and the rubyl chlorides were prepared by Rabe and Riza (Annalen, 1932, **496**, 151). These substances are of purely academic interest except as regards their stereochemical relationships to the cinchona alkaloids.

(*c*) **Stereochemistry.**—The cinchona alkaloids contain four dissimilar, asymmetric carbon atoms, marked (1) to (4) in the following formula, in which **Q** stands for the quinolyl or 6-methoxyquinolyl residue, and **R′** for the vinyl or ethyl group. Sixteen stereoisomeric forms (8 pairs of mirror-image enantiomorphs) of any one alkaloid should therefore be capable of existence. Cinchonine and cinchonidine are two such forms, but they are not an enantiomorphous pair.



Although the nitrogen atom is also unsymmetrical, it does not affect the number of possible stereoisomerides, for, when two asymmetric atoms are, directly or indirectly, linked together three times over, they constitute but one centre of dissymmetry, as can be seen with the aid of a model. This accounts, for example, for there being only two forms of camphor (Skraup, Ber. 1902, **35**, 3981 ; Rabe, *ibid.* 1922, **55**, 527).

The two problems which challenge the chemist are (1) to determine the *relative* configurations or "partial rotations" of these four atoms in the various alkaloids, and 2) to prepare, in each structural case, the 14 other possible stereoisomerides. The present position is summarised in Table II.

TABLE II.

Case.	Represented by the following alkaloids.	"Partial Rotation" of asymmetric C atoms.			
		1	2	3	4
1	Cinchonine, quinidine, and their dihydro-derivatives	+	−	+	+
2	*epi*Cinchonine, *epi*quinidine, and their dihydro-derivatives	+	−	+	−
3	*epi*Cinchonidine, *epi*quinine, and their dihydro-derivatives	+	−	−	+
4	Cinchonidine, quinine, and their dihydro-derivatives	+	−	−	−
5*	*d*-Hydroquinine (*d*-hydrocinchonidine and the corresponding vinyl alkaloids are unknown)	−	+	+	+
6†	*l*-Hydroquinidine (*l*-hydrocinchonine and the corresponding vinyl alkaloids are unknown)	−	+	−	−
7‡	Not represented by known alkaloids	−	+	+	−
8§	Not represented by known alkaloids	−	+	−	+

* enantiomorph of *case* 4
† enantiomorph of *case* 1.
‡ enantiomorph of *case* 3
§ enantiomorph of *case* 2

This information has been obtained in the following manner:

When cinchonine chloride in dilute sulphuric acid solution is reduced by means of iron filings, the halogen atom is replaced by hydrogen, and there is formed " desoxycinchonine " (Koenigs, Ber. 1895, **28**, 3143; 1896, **29**, 372). The same applies to the other naturally occurring alkaloids, a distinct desoxy-base being formed in each case. These substances are of central significance for the solution of the problem, inasmuch as in their molecules carbon atom 4, but not 3, has become symmetrical. For this reason, Rabe and his collaborators (Annalen, 1932, **492**, 242), mistrusting the validity of stereochemical arguments based on substances obtained by means of phosphorus pentachloride, prepared the desoxy-bases by a different route, *viz.* by heating the hydrazones of the cinchona-ketones (*e.g.* cinchoninonehydrazone) with powdered potash:

$$C{=}N{-}NH_2 \rightarrow CH_2 + N_2,$$

a method due to Kishner (J. Russ. Phys. Chem. Soc. 1911, **43**, 1398, and later papers). No modification of the argument, however, was necessary.

The cinchona-toxines and -ketones furnish cases in which both carbon atoms 3 and 4 are rendered inactive together, while carbon atoms 1 and 2 remain unchanged. It is this circumstance which accounts for there being only one toxine and only one ketone for any one given pair of stereoisomeric parent alkaloids. The ketones are at first sight, like the desoxy-bases, symmetrical about carbon atom 4 but not about carbon atom 3. Rabe showed, however, that while this may be the case for the solid substances, in solution enolisation occurred, and dynamic equilibrium was established between the keto- and the enol- forms: the cinchonaketones are tautomeric (Rabe, Kuliga, Marschall, Naumann and Russell, Annalen, 1910, **373**, 85). Thus the ketones are slightly soluble in strong caustic alkali solution; they form **O**-benzoyl derivatives and they exhibit mutarotation. The asymmetry of centre 3 being destroyed in the enol- form, complete racemisation of this centre, in the keto- form also, must take place in solution.

That the configuration of centres 1 and 2 is the same for all the alkaloids was foreshadowed by Pasteur (Compt. rend. 1853, **37**, 110), who observed that any one pair of stereoisomeric alkaloids was transformed to one and the same feebly dextrorotatory " -icine " (toxine). Howard (J.C.S. 1873, **26**, 1177) also noted that the optical rotatory powers of cinchonicine and of quinicine were, fairly accurately, the arithmetic means of those of cinchonine and cinchonidine, and of quinine and quinidine respectively. The extension of this argument from one stereoisomeric pair to another structurally distinct pair is made possible for all the vinyl alkaloids on the one hand, and for all the hydro-alkaloids on the other, by the fact that they all give rise to one and the same optically identical meroquinene or cincholoipon, as the case may be. These degradation products of the " second half" contain the original centres 1 and 2 intact. The stereochemical gap between the saturated and unsaturated series was first closed by Koenigs (Ber. 1902, **35**, 1350), who reduced meroquinene by means of zinc dust and cold, fuming hydriodic acid, and obtained cincholoipon, optically identical with that gained from the hydro-alkaloids by degradation. Since that time the transition from the vinyl to the hydro-alkaloids has been often effected by the method of catalytic hydrogenation.

Directly or indirectly, then, all the cinchona alkaloids give rise to one and the same cincholoipon, and so have the same configuration about centres 1 and 2, the total contribution of which is weakly dextrorotatory, as shown by the optical rotatory power of the ketones and the toxines. The individual configuration at each of these centres has been worked out recently (Henry, Solomon, and Gibbs, J.C.S. 1937, 594; 1938, 6) by a study of the isomerides of the unsaturated alkaloids formed by the action of mineral acids (*see* section (*d*) below), and the results are included in Table II. For the present purpose it will suffice to regard carbon atoms 1 and 2 as constituting a single asymmetric centre, which is dextrorotatory in total effect in the naturally-occurring alkaloids. On this basis there will be 8 stereoisomerides in any one case of a single structural type. In the hydroquinine series, 6 of these 8 cases are represented. Of these, two, *l*-hydroquinine and *d*-hydroquinidine, occur naturally; their full mirror image enantiomorphs, *d*-hydroquinine and *l*-hydroquinidine have been synthesised by Rabe and Schultze (Ber. 1933, **66**, [B], 120); the remaining two, *epi*hydroquinine and *epi*hydroquinidine, were prepared from hydroquininone by reduction, as well as from hydroquinine or hydroquinidine by treatment with amyl alcoholic potash (Rabe and others, Annalen, 1932, **492**, 242).

In spite of identity of configuration at centres 1 and 2, the stereoisomerides cinchonine and cinchonidine—to take an instance—are, nevertheless, distinct, and must therefore have opposite configurations either about carbon atom 3, or about carbon atom 4, or at both these centres. Now, the distinction between the two is preserved in the desoxy-bases; desoxycinchonine is not the same as desoxycinchonidine, although they are identical at centres 1 and 2 and also at 4, being symmetrical at the latter point. The two desoxy-bases are therefore epimeric about carbon atom 3. The same applies to the parent alkaloids, except that these may or may not be epimeric also about carbon atom 4. The ideal way to settle this last point would be by an analogous procedure. Unfortunately, however, no derivative of the cinchona alkaloids is known in which carbon atom 3 becomes symmetrical while carbon atom 4 remains unchanged.

The problem is solved by studying the reduction products of the cinchonaketones.

Carbon atoms 3 and 4 in the ketones are racemised by the dynamic equilibrium of tautomeric forms. On reduction back to the secondary alcoholic condition, however, they should resume a fixed dissymmetry. Now, the production of two new asymmetric carbon atoms in a molecule already possessed of an independent centre of dissymmetry, and optically active, should result in four non-enantiomorphous stereoisomerides; these need not necessarily be formed in equivalent proportions. The reduction of the cinchona-ketones should therefore be expected to give rise to four stereoisomeric carbinols; the original naturally occurring pair, and two others. This was first found to be the case with hydrocinchoninone (Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H., G.P. 330813, 1920), which, on reduction with aluminium or zinc in alcoholic solution and in the presence of sodium ethoxide, furnished the strongly dextrorotatory hydrocinchonine ($[\alpha]_D$ +190°), the strongly lævorotatory hydrocinchonidine ($[\alpha]_D$ −98°), and two other alkaloids, one of $[\alpha]_D$ +88·5° and the other of $[\alpha]_D$ +48°. It was then pointed out by King and Palmer (J.C.S. 1922, **121**, 2577) that, without having to use the questionable procedure of applying in a strictly quantitative sense Hudson's rule of optical superposition, it was nevertheless possible to deduce, justifiably enough, that the strongly dextrorotatory hydrocinchonine had a dextro- configuration at 3 and also at 4; that similarly, the strongly lævorotatory hydrocinchonidine had a lævo- configuration at each of those centres; while of the two new alkaloids, both of a more feeble rotatory power than either of the preceding, naturally occurring stereoisomerides, one had a dextro- at 3 and a lævo- configuration at 4, and the other, *vice versa*, was *dextro-* at 4 and *lævo-* at 3. The argument was generalised by analogy to all the cinchona alkaloids, but it was pointed out that, on the evidence, it was impossible to establish the constitution of the new "hydrocinchonines."

The justification for that generalisation, and the identification of each of the new "*epi*-bases" was furnished by Rabe, Irschick, Suszka, Müller, Nielsen, Kolbe, von Riegen and Hochstätter (Annalen, 1932, **492**, 242). All the "*epi*-bases" (*see* Table II) were prepared, on the one hand, by reduction of the ketones, as had been done in the Zimmer patent with hydrocinchoninone, and on the other hand, by epimerisation of the parent alkaloids by means of amyl alcoholic potash. For, in the latter process, it was found, for example, that cinchonine gave rise not only to cinchonidine (Koenigs and Husmann, Ber. 1896, **29**, 2185), but to a mixture in dynamic equilibrium of all four stereoisomerides in question—cinchonidine, *epi*cinchonidine, *epi*cinchonine, and unchanged cinchonine. It was found, in experimental verification of King and Palmer's analogical generalisation, that the two most feebly rotating substances in any one group of four stereoisomerides were the new "*epi*-bases."

Finally, all the new alkaloids were identified by conversion to the chlorides, and reduction of these to the desoxy-bases in each case. In each group of four, one "*epi*-base" gave rise to one previously known desoxy-base, and the other to the other. In the case of cinchonine, cinchonidine, and their two new congeners, for example, one of the latter gave rise to desoxycinchonine; it was hence identified as *epi*cinchonine (+ at 3; − at 4); the other furnished desoxycinchonidine, and was assigned its position as *epi*cinchonidine (− at 3; + at 4). This relation is illustrated below.

Dextro-configuration at 3.

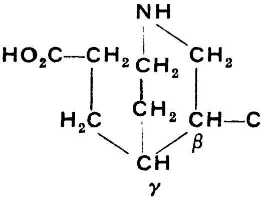
Cinchonine (+224·4°; + at 4) | *epi*Cinchonine (+120·3°; − at 4)
↓ ↓
Desoxycinchonine
(4-symm.)

Lævo-configuration at 3.

*epi*Cinchonidine (+62·8°; + at 4) | Cinchonidine (−111°; − at 4)
↓ ↓
Desoxycinchonidine
(4-symm.)

The synthesis of the optical antipodes of hydroquinine and of hydroquinidine (Cases 5 and 6 in Table II) was effected by Rabe and Schultze (*l.c.*) by precisely the same method whereby, as already explained their naturally occurring stereoisomerides had been synthesised two years earlier.

The β- and γ-carbon atoms of *homo*cincholoipon (which had then been synthesised, and formed one of the last stages in the main synthesis) are unsymmetrical, and constitute carbon atoms 1 and 2 respectively in the subsequent cinchona molecule. *homo*Cincholoipon can therefore exist in two racemic modifications, and both were in fact formed. Of the resolved, optically active components of one of these forms, one, obtained by means of *d*-tartaric acid, has proved to be identical with *d*-*homo*cincholoipon (*i.e.* with that obtained by the oxidation of benzoylhydrocinchotoxine). The other, its lævo-enantiomorph, obtained similarly by means of *l*-tartaric acid, was esterified and, in the form of its N-benzoyl-derivative, was now condensed with quininic ester exactly as before. Carbon atoms 1 and 2 in the resulting hydroquinotoxine therefore were lævorotatory in combined effect. This new hydroquinotoxine was then converted to a new hydroquininone as before, which, on reduction, gave rise to a mixture of carbinols containing presumably four stereoisomerides. Of these, only *d*-hydroquinine and *l*-hydroquinidine, however, were isolated. They were identical in all respects with the naturally occurring *l*-hydroquinine and *d*-hydroquinidine respectively, except that they



*homo*Cincholoipon.

had opposite signs of rotation. Numerically the rotations of the new enantiomorphs were respectively equal to those of hydroquinine and hydroquinidine. On admixture, each pair of enantiomorphs formed a racemic, optically inactive compound.

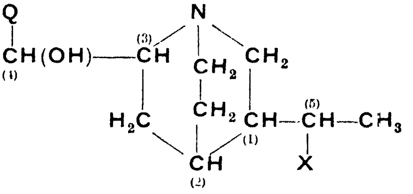
The other stereoisomeric *homo*cincholoipons, also present in Rabe's crude synthetic product, were not isolated. They would form the starting material for a synthesis of cinchona alkaloids in which carbon atoms 1 and 2 would have configurations differing, *relatively to one another*, from that present in the natural bases. These other *homo*cincholoipons would provide a route to synthesis of some of the isomerides, which enabled Henry, Solomon and Gibbs (*l.c.*) to propose separate configurations for carbon atoms 1 and 2, and a discussion of which follows.

(*d*) **Behaviour with Mineral Acids.**—A broad distinction between the hydro-alkaloids and those of the unsaturated series is that the former are substances which are relatively stable and indifferent to the action of strong mineral acids. These reagents serve, at most, to demethylate the methoxylated hydro-alkaloids, hydroquinine and hydroquinidine, to hydrocupreine and hydrocupreidine respectively.

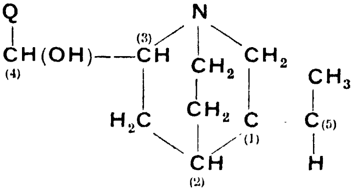
The unsaturated alkaloids, on the contrary, when treated with mineral acids, sometimes even under relatively mild conditions, undergo a series of changes the nature of which has been and, to a smaller extent, still is a vexed problem in the history of these alkaloids. The difficulty is to some extent an experimental one. The reaction usually gives rise not to a single substance, but to a variety of products which are difficult to separate ; many have a marked tendency to form with one another loose compounds which behave as single substances. Some, particularly the phenolic bases derived from quinine and quinidine, are difficult to crystallise and to characterise owing to instability in the air, or to indefiniteness of melting-point, or owing to the fact that they undergo slow decomposition on drying for analytical purposes.

This problem is still receiving active attention in several laboratories, but enough is now known to warrant the following tentative account, even though it may require modification in the near future. For this reason also, and in view of the complexity of the subject, it will be more convenient not to encumber the discussion with references either to particular cases or to the experimental evidence. The bibliography of the literature on which this account is based will be found at the end of this section.

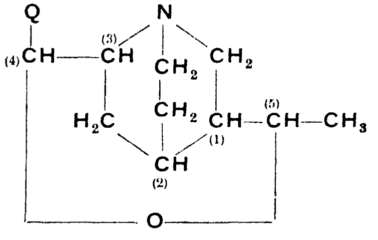
Three distinct types of substance may be produced when the unsaturated cinchona alkaloids are treated with mineral acids. The first type (A) arises from the addition of the elements of the reagent to the double bond. The other two types result from the isomerisation of the parent alkaloids by (B) wandering of the double bond, and (C) loss of the double bond by intramolecular ether formation involving the central hydroxyl group. In addition, the methoxylated alkaloids, quinine and quinidine, undergo demethylation when the action is sufficiently drastic ; the phenolic bases *apo*quinine, *apo*quinidine, and their congeners are then formed. The three types have had assigned to them the following structural formulæ respectively, which are probably substantially correct :



Type A.



Type B.



Type C.

Q stands for the quinolyl-, 6-hydroxy- or methoxyquinolyl residue.

A fourth type of substance is also formed. This cannot, however, be considered here, as no general agreement has as yet been reached concerning its structure. This fourth type is represented by " δ-cinchonine " (" α- and β-cinchonhydrine ") from cinchonine, " niquine " from quinine, and " niquidine " from quinidine.

Substances of type A (X = halogen) are formed to the exclusion of the other types when any vinyl alkaloid is treated with very concentrated hot or cold halogen hydracid (*e.g.* hydrochloric acid, saturated at −17°). The same substances are also produced when any of the transformation products, A (X = —OH), B, or C, are treated in similar fashion, except that a higher temperature is then requisite.

When the acids are dilute and hot (*e.g.* hydrochloric acid of sp.gr. 1·125 at 140°), or when sulphuric acid (50% and upwards) is used instead of the halogen acids, all three types are formed side by side, except that in the case of the lævorotatory alkaloids, cinchonidine and quinine, type C is absent. This statement also applies either to the parent alkaloids or to any of the transformation products under discussion, although the results in the two cases are rarely identical. When sulphuric acid is used, type A is formed by the addition of the elements of water to the vinyl group ($X = —OH$).

ACTION OF HOT, DILUTE HALOGEN HYDRACIDS OR OF SULPHURIC ACID ON THE CINCHONA ALKALOIDS.

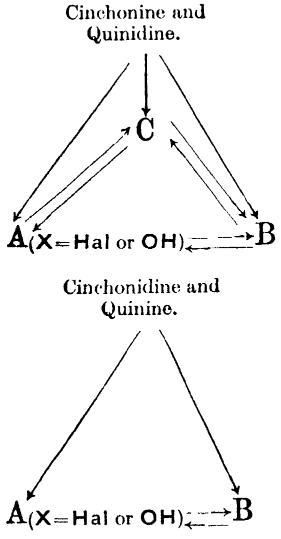


Diagram 1.

The isomeride types (B and C) can be formed not only as described, but also by the abstraction of a molecule of hydrogen halide from the halogenohydro-cinchona alkaloids of type A. The reaction is effected either by means of alkali, or silver salts, or by heating the bases in alcoholic or aqueous-alcoholic or in benzene solution. It is this reaction which gives rise to the "δ-cinchonine," "niquine," and "niquidine" mentioned above. Otherwise, only substances of types B and C are formed; substitution of the halogen for another group, producing variants of type A with $X = —OH, —OCH_3, —O—CO—CH_3$ or NH_2, has never been observed. The mild nature of the media (neutral or alkaline, but never acid) used for the dehalogenation suggests the possibility of the regeneration of the vinyl group, *i.e.* of the parent alkaloid, and it has been claimed several times that this does in fact occur. The present author, however, is doubtful whether, for example, quinine and cinchonine, have ever been regenerated from their addition compounds with the halogen hydracids.

This alternative method of preparing the isomeride-types resembles the mineral acid procedure already described, in this case also the lævorotatory alkaloids, cinchonidine and quinine, fail to give rise to type C. Type C is in fact never formed from the lævorotatory alkaloids and is unknown, because in the lævorotatory series the central hydroxyl and vinyl groups are remote, whereas in the dextro-series they are close together. This circumstance is determined not, as might at first sight be supposed, by the configuration of carbon atom 4, but by that of carbon atom 3, as can be readily seen with the aid of a model.

Stereochemistry. *Type A.*—Whereas the parent cinchona alkaloids contain four asymmetric carbon atoms, and should be capable of existing in 16 stereoisomeric forms, substances of type A contain five such atoms, and should therefore give rise to 32 stereoisomerides. The new asymmetric atom (marked 5 in the formula) is the one to which the group X becomes attached. Any one parent alkaloid should therefore give rise to two structurally identical forms of type A. Two forms of hydroxy- and halogeno- hydro-cinchona alkaloids are, in fact, known in many cases.

Type B.—This type contains a double bond between asymmetric carbon atoms 1 and 5, and is capable of geometrical isomerism. Any one known[1] parent alkaloid should therefore give rise to two forms of this type—one *cis* and one *trans*. This, also, is in accord with the experimental evidence.

Type C.—Stereochemically, this is the most abstruse type of the three. In common with type A, it contains five asymmetric carbon atoms; it can, nevertheless, only give rise to 16 stereoisomeric forms. As was pointed out in the last section, although carbon atom 2 and the nitrogen are both asymmetric, they nevertheless constitute only a single effective asymmetric centre, for the reason that they are the terminals of a *p*-bridge in a bicyclic system. In the C-type, carbon atoms 1 and 3 are another such pair, the bridge being

$$—C^{5}HMe—O—C^{4}HQ—.$$

There are, therefore, only four effective asymmetric centres in the molecule. This circumstance is made manifest by the inability, already noted, of the lævorotatory alkaloids to form this type; the lævorotatory alkaloids differ from their dextrorotatory isomerides in respect of the configuration at carbon atom 3. Each of the eight possible parent forms of the cinchona alkaloids which has a dextro-configuration at carbon atom 3 can, therefore, give rise to two stereoisomeric forms of type C.

In effect, therefore, any one parent unsaturated cinchona alkaloid, when it can give rise to a given type, can give rise to two stereoisomeric forms of that type. This statement applies to all three types, but requires qualification in the case of type C. For although cinchonine gives rise to two forms of the bridged type, *viz.* α- and β-*iso*cinchonines, a circumstance which should be accounted not so much a verification of stereochemical theory as a defect in the search for other forms, quinidine, the stereochemical analogue of cinchonine, furnishes three *iso*-quinidines having the O-bridge structure.

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[1] The same actually applies to any one of the 16 possible parent forms [*see* section 5 (*c*), *above*], whether known or unknown. Although there are, nevertheless, not 32 but only 16 B-forms possible, the above statement is correct as far as it goes. The resolution of the apparent contradiction must be left to those interested, because, belonging to a somewhat recondite field of stereochemistry, it would be outside the scope of this article. A full explanation, moreover, would not be germane to the discussion.

No two parent alkaloids are known to give rise to any one and the same transformation product. It is assumed, therefore, that the configurations of the four asymmetric carbon atoms originally present are not affected by treatment with acids, and that the transformation products derived from other possible, but still unknown, parent types would similarly occur in distinct sets.[1] The existence of three *iso*quinidines of one type renders this assumption untenable, at all events in the case of type C. The third *iso*quinidine is not derived from quinidine, but probably from a stereoisomeride.

The following bibliography, on which the foregoing account of the behaviour of the cinchona alkaloids towards mineral acids is based, is arranged on a chronological basis of authors. The publications of any one author and his collaborators are not interspersed with those of other authors, so that the order of the entire list is not chronological. The authors are listed in order of date of the earliest publication:

Zorn (J. pr. Chem. 1873, [ii], **8**, 279); Hesse (Annalen, 1880, **205**, 314; 1888, **243**, 131; 1890, **260**, 213; 1892, **267**, 138; 1893, **276**, 88, 125); Julius (Monatsh. 1884, **6**, 750); Comstock and Koenigs (Ber. 1887, **20**, 2510); Koenigs (Annalen, 1906, **347**, 184); Jungfleisch and Léger (Compt. rend. 1887, **105**, 1255; 1888, **106**, 68, 357, 657, 1410; 1889, **108**, 952; 1891, **113**, 651; 1892, **114**, 1192; 1893, **117**, 42; 1894, **118**, 29, 536; 1894, **119**, 1268; 1895, **120**, 325; 1901, **132**, 410, 828; Ann. Chim. 1920, **14**, 59); Léger (Compt. rend. 1918, **166**, 76, 469, 903; 1919, **168**, 404; 1919, **169**, 67, 797; J. Pharm. Chim. 1936, **23**, 558); Lippmann and Fleissner (Ber. 1891, **24**, 2827; 1893, **26**, 2005; Monatsh. 1891, **12**, 327; 1893, **14**, 371; 1895, **16**, 34); Skraup (Monatsh. 1891, **12**, 431; with Schubert, Monatsh. 1891, **12**, 669; Ber. 1892, **25**, 2909; Monatsh. 1893, **14**, 428; 1897, **18**, 411; 1899, **20**, 571, 585; 1900, **21**, 512; with Zwerger, Monatsh. 1900, **21**, 535; 1902, **23**, 455; 1904, **25**, 894; Monatsh. 1901, **22**, 171, 253, 1083, 1097; 1903, **24**, 291, 311; with Egerer, Monatsh. 1903, **24**, 669); Pum (Monatsh. 1891, **12**, 582; 1892, **13**, 676; 1895, **16**, 68); Neumann (Monatsh. 1892, **13**, 651); Cordier von Löwenhaupt (Monatsh. 1898, **19**, 461); von Arlt (Monatsh. 1899, **20**, 425); Langer (Monatsh. 1901, **22**, 151, 157); Hlavnička (Monatsh. 1901, **22**, 191); Widmar (Monatsh. 1901, **22**, 976); Kaas (Monatsh. 1904, **25**. 1145; 1905, **26**, 119); Pfannl (Monatsh. 1911, **32**, 241); Paneth (Monatsh. 1911, **32**, 257); Böttcher and Horowitz (Monatsh. 1911, **32**, 793; 1912, **33**, 567); Rabe and Böttcher (Ber. 1917, **50**, 127); Rosenmund and Kittler (Arch. Pharm. 1924, **262**, 18); Giemsa and Bonath (Ber. 1925, **58**, [B], 87); Fränkel and Buhlea (Ber. 1925, **58**, [B[, 559); Suszko *et al.* (Bull. Acad. Polonaise, A. 1925, 129; 1929, 340; 1933, 119; 1935, **65**, 360, 415, 457, 465; Rocz. Chem. 1933, **13**, 360, 464; Rec. trav. chim. 1933, **52**, 839, 847; 1935, **54**, 481; 1936, **55**, 392); Henry (with Solomon, J.C.S. 1934, 1923; with Solomon and Gibbs, *ibid.* 1935, 966; 1937, 592); Goodson (J.C.S. 1935, 1094); Solomon (*ibid.* 1938, 6).

6. Properties of Individual Substances.—The following list, designed to give more detailed information concerning the discovery, occurrence, and properties of the individual alkaloids and their derivatives, is arranged in alphabetical order of the naturally occurring alkaloids (p. 128). After each description of an alkaloidal base there follow descriptions of its principal salts and derivatives, and the more important of its transformation and degradation products.

Aricine (quinovatine), $C_{23}H_{26}O_4N_2$, named after the port of Arica in Peru, was discovered in Cusco bark (*C. Pelletierana*) by Pelletier and Corriol (J. Pharm. Chim. 1829, **15**, 575). It forms large, colourless prisms from alcohol, m.p. 188°, $[\alpha]_D^{15}$ $-58{\cdot}2°$ ($c=2$ in 97% alcohol), but $+14{\cdot}5°$ in acid solution. It is soluble at 15° in 100 parts of 90% alcohol, or 33 parts of ether, very soluble in chloroform and insoluble in water. With concentrated sulphuric acid it gives a greenish-yellow colour, changing to deep blue on addition of ammonium molybdate, and this becomes olive-green on warming. This colour reaction is also characteristic of cusconine. Nitric acid produces a deep green coloration, and affords a greenish-yellow solution. Aricine is astringent but not bitter in taste. It is a weak base, and its salts dissociate in water.

The *hydrochloride*, $B{\cdot}HCl,2H_2O$. forms colourless prisms, slightly soluble in cold water. The *sulphate*, $B_2{\cdot}H_2SO_4$, consists of fine needles, fairly soluble in cold water. The acid sulphate, $B{\cdot}H_2SO_4$, is less soluble. Aricine also forms an acetate, a citrate, a hydriodide, and two oxalates, the "*binoxalate*," $B{\cdot}C_2H_2O_4,2H_2O$, being very sparingly soluble in cold water. The platinichloride, salicylate, and thiocyanate are also described (Hesse, Annalen, 1878, **185**, 296; Moissan and Landrin, J. Pharm. Chim. 1890, **21**, 337).

Chairamidine, $C_{22}H_{26}O_4N_2$, was isolated from the bark of *Remijia Purdieana* by Hesse (Annalen, 1884, **225**, 253). It is accompanied in the bark by a series of other alkaloids, and is isolated by first removing these as sulphates, hydrochlorides or thiocyanates. For details of the method Hesse's paper should be consulted. Chairamidine is a white, amorphous powder containing $1H_2O$. The anhydrous substance has m.p. 126°-128° (decomp.), and $[\alpha]_D^{15}$ $+7{\cdot}3°$ ($c=3$ in 97% alcohol). It is insoluble in water, and readily soluble in alcohol, ether, chloroform or benzene. It dissolves in concentrated sulphuric acid to a yellow solution, which slowly turns green. Animal charcoal removes it completely from a solution in acetic acid. Chairamidine is a weak base, and its solutions in alcohol are neutral to litmus. Its salts are amorphous.

Chairamine, $C_{22}H_{26}O_4N_2$, also occurs in *Remijia Purdieana* (Hesse, Annalen, 1884, **225**, 243), and is obtained as the hydrochloride from the mother-liquors remaining after removing the concusconine as sulphate. The base crystallises with $1H_2O$ from dilute alcohol (slender white needles) or from strong alcohol (thick prisms). The hydrate melts at 140°, and the anhydrous base at 233°; $[\alpha]_D$ about $+100°$ in 97% alcohol.

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[1] But in the case of type B, *see* footnote on page 150.

It is soluble at 11° in 540 parts of 97% alcohol, but is readily soluble in ether or chloroform. It dissolves to a colourless solution in concentrated sulphuric acid, but this slowly turns dark green. This colour is also produced when concentrated nitric acid is added to a solution of chairamine in acetic acid. In addition to the crystalline hydrochloride used for its separation, a *sulphate*, $B_2\cdot H_2SO_4,8H_2O$, is also known.

Cinchamidine.—*See* Hydrocinchonidine.

Cinchona Febrifuge.—*See* Quinetum.

Cinchonamine, $C_{19}H_{24}ON_2$, was isolated by Arnaud (Compt. rend. 1881, **93**, 593; 1883, **97**, 174). It occurs in the bark of *Remijia Purdieana* together with cinchonine, concusconine, chairamine, chairamidine, conchairamine, and conchairamidine. Hesse (Annalen, 1884, **225**, 211, 218) gives a scheme of separation. The cinchonamine is purified by taking advantage of the insolubility of its nitrate. The base crystallises from alcohol in needles or orthorhombic, triboluminescent prisms, m.p. 184°–185° (Hesse), 195° (Arnaud), $[\alpha]_D^{15}$ +121·1° (c=2 in 97% alcohol). It is almost insoluble in cold water, but slightly soluble in hot water, from which it crystallises in short prisms. Cinchonamine dissolves in 31·6 parts of 90% alcohol at 17°, and in 100 parts of ether. It is also soluble in chloroform, benzene, light petroleum or carbon disulphide. Cinchonamine is said to be toxic, but more powerfully antipyretic than quinine. Its solutions do not fluoresce, neither do they give the thalleioquin reaction. It differs from its isomerides, hydrocinchonine and hydrocinchonidine, in being readily attacked by potassium permanganate. Cinchonamine does not contain a methoxyl group, but forms a methiodide and an acetyl-derivative. With nitric acid it forms a yellow, amorphous, explosive dinitro-derivative.

Cinchonamine is a strong diacidic base which forms well-defined salts. Of greatest interest is the *nitrate*, $B\cdot HNO_3$ (minute prisms, m.p. 196°), the insolubility of which is found useful, as already stated, in purifying this alkaloid. Arnaud (Ann. Chim. 1890, **19**, 93) proposed the use of cinchonamine for the estimation of nitrates, but the method is limited in its application (Howard and Chick, J.S.C.I. 1909, **28**, 53). The *hydrochloride*, $B\cdot HCl$, soft laminæ, or $B\cdot HCl,H_2O$, transparent cubical crystals, is soluble in 200 parts of water at 27° (Howard and Perry, *ibid.* 1905, **24**, 1281). The *sulphate*, $B_2\cdot H_2SO_4$ (prisms), in contradistinction to a number of cinchona alkaloids, is very soluble in water, as is also the *acid sulphate*, $B\cdot H_2SO_4$ (octahedra or prisms). The citrate, hydrobromide, hydriodide, malate, platinichloride, picrate, tartrate, and thiocyanate are also known. Boutroux and Genvresse (Compt. rend. 1897, **125**, 467) have described a series of crystalline double chlorides with cadmium, zinc and copper.

Cinchonicine.—*See* Cinchotoxine *under Cinchonine.*

Cinchonidine, $C_{19}H_{22}ON_2$, occurs naturally in most cinchona barks, and particularly in *C. succirubra*. It can also be obtained artificially by treating cinchonine with amyl alcoholic potash (Koenigs and Husmann, Ber. 1896, **29**, 2185). It was first isolated from *C. tucujensis* by Winckler (Jahresbericht, 1847/1848, 620), who called it "quinidine." It was renamed "cinchonidine" by Pasteur (J. Pharm. Chim. 1853, **23**, 123), who suspected that the new alkaloid was isomeric with cinchonine. The confusion which resulted in the literature may be regarded as typical of the uncertainty, which existed in the middle of last century, concerning the identity of several cinchona alkaloids (*see, e.g.* Hesse, Annalen, 1865, **135**, 334; 1873, **166**, 243; 1875, **176**, 322; Ber. 1877, **10**, 2149, 2152). The identity of cinchonidine was finally placed on a satisfactory basis by Skraup and Vortmann (Annalen, 1879, **197**, 226), who also gave it the correct empirical formula. It is isolated (from the mother-liquors from quinine sulphate) as tartrate, and purified either as neutral sulphate (Hesse, Annalen, 1880, **205**, 196), or as acid sulphate; for the preparation of the latter, each gram of crude, dry cinchonidine base is dissolved in 2·1 c.c. of 50% sulphuric acid and 11 c.c. of alcohol. The base is finally recovered and recrystallised from alcohol. The product so obtained still contains some quinine and hydrocinchonidine, which can be removed by recrystallisation from benzene, and fractional crystallisation from alcohol respectively (Buttle, Henry, and Trevan, Biochem. J. 1934, **28**, 436).

Cinchonidine crystallises in anhydrous, large trimetric prisms, or thin plates. Its melting-point has been given variously, ranging from 202° to 210·5°; the melting-point given by Buttle, Henry, and Trevan (*ibid.* p. 438) for their pure cinchonidine is 204·5°. It is lævorotatory: $[\alpha]_D^{17\cdot8}$ −107·9° (c=1 in 1 vol. alcohol+2 vols. chloroform) (Lenz, Z. anal. Chem. 1888, **27**, 563); −86·2° (c=1·0955 in chloroform) (Rabe *et al.*, Annalen, 1910, **373**, 100); −111·0° (c=0·878 in 99% alcohol) (Rabe, *l.c.*); −178° (c=0·735, *i.e.* *M*/40 solution in 0·1N-H_2SO_4) (Buttle *et al.*, *l.c.*). Cinchonidine is almost insoluble in water (1 in over 5,000); it dissolves in 300 parts of cold alcohol (sp.gr. 0·935) or in 16 parts of 97% alcohol; in over 1,000 parts of dry ether, but in 188 parts of ether sp.gr. 0·72. It is readily soluble in chloroform or amyl alcohol. Cinchonidine solutions neither fluoresce nor give the thalleioquin reaction (distinction from quinine and quinidine). The alkaloid is distinguished from its stereoisomeride, cinchonine, in being lævorotatory, in its greater solubility in ether, and by giving an insoluble tartrate. On oxidation with potassium permanganate it gives rise to cinchotenidine (*see* p, 154*b*), and with chromic acid it is degraded to the same substances that are formed from cinchonine in like manner. On reduction with hydrogen in the presence of platinum or palladium catalysts, hydrocinchonidine (*q.v.*) is formed. Cinchonidine gives rise to the same cinchotoxine (cinchonicine) that is formed from cinchonine.

Cinchonidine Sulphate, $B_2\cdot H_2SO_4$, crystallises from cold water in needles containing $6H_2O$, from hot water in needles containing $3H_2O$, and from alcohol with $2H_2O$. The salt becomes anhydrous at 100° (m.p. 205°, *decomp.*), and reabsorbs $2H_2O$ on exposure. At 15° the salt is soluble in 100 parts of water, 60 of alcohol, or 1,000 of chloroform ; at 25° it dissolves in 63 parts of water or 72 of alcohol. The solubility in water at 80° is threefold that at 25°.

Cinchonidine Acid Sulphate, $B\cdot H_2SO_4,5H_2O$, is readily soluble in water; $[\alpha]_D^{15}$ $-133\cdot6°$ (c=0·98 of anhydrous salt, *i.e.* an $M/40$ solution, in water). The same rotation is observed in $M/10$ solution, and in 0·1N-H_2SO_4. The *tetra-sulphate*, $B\cdot 2H_2SO_4,H_2O$, is slowly soluble in water.

Cinchonidine Hydrochloride, $B\cdot HCl,H_2O$, forms monoclinic prisms from water. It crystallises from alcohol in fine needles containing $2H_2O$. The anhydrous salt has m.p. 242°; $[\alpha]_D^{20}$ $-117\cdot6°$ (c=1·214 in water). The salt is soluble at 12° in 30 parts of water, and in 300 parts of ether; it dissolves readily in alcohol or in chloroform.

Cinchonidine Tartrate, $B_2\cdot C_4H_6O_6,2H_2O$, forms fine needles soluble in 1,265 parts of water at 10°, and almost insoluble in sodium potassium tartrate solution.

Other known salts of cinchonidine include the dihydrochloride, hydrobromide, dihydrobromide, hydriodide, dihydriodide, nitrate, oxalate, acid tartrate, benzoate, salicylate and succinate. A number of double compounds with metallic salts have been described.

Cinchonidine Methiodide, $C_{19}H_{22}ON_2\cdot CH_3I$, is formed from the components in alcoholic solution at room temperature (24 hours). Fine colourless needles, m.p. 248° (Claus and Bock, Ber. 1880, **13**, 2192).

Acetylcinchonidine, $C_{19}H_{21}(CO\cdot CH_3)ON_2$, results from the action of acetic anhydride at 60°–80°. Amorphous powder (Hesse, Annalen, 1880, **205**, 319; Hilditch, J.C.S. 1911, **99**, 238).

α-Chlorohydrocinchonidine, better α-chlorodihydrocinchonidine (component of "hydrochlorocinchonidine"),

$$C_9H_6N\text{-}CH(OH)\text{-}C_7H_{11}N\text{-}CHCl\text{-}CH_3,$$

is obtained by the action of hydrochloric acid, either at room temperature with acid saturated at −17°, or at 85° with the ordinary concentrated acid. It is isolated from the products of the reaction as acid sulphate or tartrate, and then fractionated as dihydrobromide when it forms the more soluble component. The base (from alcohol) has m.p. 231° (*decomp.*), $[\alpha]_D^{23}$ $-135\cdot6°$ (c=0·5 in N-HCl) (Goodson, J.C.S. 1935, 1096).

The more sparingly soluble component in the dihydrobromide fractionation is *α′-chlorohydrocinchonidine*, which is epimeric with the α-derivative at the carbon atom carrying the chlorine atom. The α′-derivative (base) crystallises from alcohol, has m.p. 246° and $[\alpha]_D^{23}$ $-62\cdot5°$ (c=0·5 in N-HCl). Its acid sulphate, tartrate and dihydrobromide are also described (Goodson, *ibid.* p. 1097).

Iodohydrocinchonidine, better iododihydrocinchonidine (hydroiodocinchonidine),

$$C_9H_6N{-}CH(OH){-}C_7H_{11}N{-}CHI{-}CH_3,$$

is obtained by heating cinchonidine with hydriodic acid (sp.gr. 1·7) on the water-bath. The base has m.p. 166° (Neumann, Monatsh. 1892, **13**, 651).

apo*Cinchonidine* (Hesse, Léger), *β-cinchonidine* (Hesse, Neumann, Léger), *γ-cinchonidine*, iso*cinchonidine* (Hesse, Paneth),

$$C_9H_6N{-}CH(OH){-}C_6H_{10}N{>}C{=}CH{-}CH_3$$

These four names have been used by the authors, whose names are bracketed after them, to designate a series of eight substances, the modes of formation and characters of which are assembled in the following table. Most probably only two pure substances, which are geometrical isomerides with the constitution indicated, are involved; some, if not all, of the eight varieties described (Table III, p. 154), may be mixtures in differing proportions.

The cinchonidine isomerides form monoacetyl derivatives and react with concentrated halogen hydracids to give the same halogenohydrocinchonidines as are obtained from the parent alkaloid.

Hydroxyhydrocinchonidine, better, hydroxydihydrocinchonidine,

$$C_9H_6N\text{-}CH(OH)\text{-}C_7H_{11}N\text{-}CH(OH)\text{-}CH_3,$$

is formed together with β- and *apo*cinchonidine in the sulphuric acid method of Léger (Bull. Soc. chim. 1919, [iv], **25**, 575). Like these, it crystallises from dilute alcohol, but it forms a diacetyl-derivative. Hydroxyhydrocinchonidine has m.p. 242°–243°, and $[\alpha]_D^{22}$ $-101\cdot7°$ in alcohol.

epi*Cinchonidine*, $C_{19}H_{22}ON_2$, is epimeric with cinchonidine about the carbinol ($CH\cdot OH$) group. It is obtained either by heating cinchonine with amyl alcoholic potash (300 g. alkaloid, 150 g. KOH, 5·5 litres amyl alcohol), or by reducing cinchoninone (100 g.) dissolved in a solution of sodium (84 g.) in alcohol (2,280 c.c.), with aluminium powder (84 g.). The *epi*cinchonidine is isolated from the ether-soluble fraction of the stereo-isomerides formed, with the aid of tartaric, dibenzoyl- and dianisoyl-tartaric acids. It forms small, colourless plates from ether, m.p. 103°–104°, $[\alpha]_D^{20}$ $+62\cdot8°$ (c=0·8044 in alcohol), is readily soluble in the usual organic solvents, and is non-fluorescent (Rabe and others, Annalen, 1932, **492**, 253.)

Cinchonidine Chloride,

$$C_9H_6N{-}CHCl{-}C_7H_{11}N{-}CH{=}CH_2,$$

is formed when anhydrous cinchonidine hydrochloride (33 g.) dissolved in chloroform (300 c.c.) is slowly treated with phosphorus pentachloride 50 g.), care being taken to avoid any rise in temperature by cooling with water. The product crystallises from a mixture of ether and ligroin (b.p. 40°–50°) in white crystals, m.p. 108°, $[\alpha]_D^{13}$ $+78\cdot2°$ (c=2·020 in 99% alcohol); $+90\cdot9°$ (c=2·009 in chloroform). The hydrochloride, $C_{19}H_{21}N_2Cl\cdot HCl$, has $[\alpha]_D^{24}$ $+24\cdot16°$ (c=1·573 in water) (Comstock and Koenigs, Ber. 1884, **17**, 1987; Rabe, Kuliga, Marschall, Naumann and Russell, Annalen, 1910, **373**, 103).

Desoxycinchonidine,

$$C_9H_6N{-}CH_2{-}C_7H_{11}N{-}CH{=}CH_2,$$

is prepared from cinchonidine chloride. A 5% solution of the chloride (12 g.) in 10% sulphuric

TABLE III.

Name.	Manner of Formation from Cinchonidine.	M.p.	$[\alpha]_D$.	Author and Reference.
*apo*Cinchonidine	Heating with 3 parts HCl (sp.gr. 1·125) at 140°–150° for 6–10 hours.	225°	−129·2° in alcohol −160·4° in dil. HCl.	Hesse, Annalen, 1880, **205**, 323, 327.
*apo*Cinchonidine	Boiling with 4 parts of 50% H_2SO_4 for 48 hours.	254·7 to 256·7°	−134·4° in alcohol. −166·6° in dil. HCl. −139·3° in alcohol-chloroform.	Léger, Bull. Soc. chim. 1919, [iv], **25**, 574.
β-Cinchonidine	Heating with 3 parts HCl (sp.gr. 1·125) at 140°–150° for 6–10 hours.	206° to 207°	−181·4° in dil. HCl.	Hesse (*l.c.*).
β-Cinchonidine	From iodohydrocinchonidine and alcoholic KOH.	244°	−171·5° in alcohol.	Neumann, Monatsh. 1892, **13**, 655.
β-Cinchonidine	Boiling with 4 parts of 50% H_2SO_4 for 48 hours.	240° to 241°	−126·6° in alcohol. −181·5° in dil. HCl.	Léger, Bull. Soc. chim. 1919, [iv], **25**, 573.
γ-Cinchonidine	From iodohydrocinchonidine and alcoholic $AgNO_3$.	238°	−164·6° in alcohol.	Neumann, Monatsh. 1892, **13**, 659.
*iso*Cinchonidine	Solution in cold conc. H_2SO_4.	235°		Hesse, Annalen, 1888, **243**, 149.
*iso*Cinchonidine	Heating with 6 vols. of 25*N*-H_2SO_4 at 100° for 2 hours.	252°	−128° in alcohol-chloroform.	Paneth, Monatsh. 1911, **32**, 259, 269.

acid is shaken with iron filings (17 g.) for 72 hours. The product crystallises from ligroin, has m.p. 60°–62°, and $[\alpha]_D^{13}$ −29·9° (c=2·006 in 99% alcohol); or −19·7° in chloroform. On treatment with alcoholic potash it gives rise to cinchene (*see under* cinchonine) (Koenigs, Ber. 1896, **29**, 373; Rabe *et al.*, Annalen, 1910, **373**, 106).

Cinchotenidine,

$$C_9H_6N—CH(OH)—C_7H_{11}N—CO_2H,$$

and formic acid are formed when cinchonidine is oxidised with potassium permanganate (Skraup and Vortmann, Annalen, 1879, **197**, 235; Hesse, Ber. 1881, **14**, 1892). It crystallises from alcohol in feathery crystals, or from water in monoclinic prisms containing $3H_2O$. It has m.p. 256° (decomp.), $[\alpha]_D^{15}$ −201·4° (c=5 in water containing 3 equivalents of HCl), is sparingly soluble in cold water, readily so in hot, and dissolves in 600 parts of boiling alcohol. It is soluble in acids as well as in caustic alkalis and is precipitated from the latter by carbon dioxide. Cinchotenidine is non-fluorescent.

Cinchonine, $C_{19}H_{22}ON_2$, was first isolated in the pure condition by Pelletier and Caventou (Ann. Chim. 1820, **15**, 295). It occurs in all cinchona barks, one of the best sources being *Cinchona Micrantha*. For purposes of quinine manufacture it ranks as a by-product and can be readily obtained from the crude mother-liquors from which quinine sulphate has been crystallised, by taking advantage of its sparing solubility in ether and in alcohol. The cinchonidine is first removed as tartrate, the mixed residual bases treated repeatedly with alcohol or ether, and the insoluble cinchonine either recrystallised from boiling alcohol or converted into sulphate and recrystallised from water. The cinchonine is finally recrystallised from alcohol several times to remove traces of quinidine. The alkaloid so prepared (adaptation of a method given by Hesse, Annalen, 1862, **122**, 227) contains about 15% of hydrocinchonine which can be removed by fractional crystallisation of the dihydrobromides, cinchonine dihydrobromide being the more soluble component (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 437) or by Thron and Dirscherl's method (Annalen, 1935, **515**, 252). Although the correct empirical formula was given by Laurent in 1848 (Ann. Chim. 1848, **19**, 365), the formula, $C_{20}H_{24}ON_2$, proposed by Regnault in 1838 (Annalen, 1838, **26**, 15) was current until 1879 when Skraup (Annalen, 1879, **197**, 353) finally showed that Laurent's formula must be adopted. Cinchonine crystallises from alcohol or from ether in prisms, the recorded melting-point is very variable, and depends on the rate of heating (Hesse, Annalen, 1880, **205**, 213, footnote); it is given as 255·4° (Lenz, Z. anal. Chem. 1888, **27**, 572), 254° (Buttle, Henry and Trevan, *l.c.*), 264·3° (Jungfleisch and Léger, Compt. rend. 1901, **132**, 830), and 268·8° (Skraup, Annalen, 1879, **197**, 355). It is dextrorotatory, the mean of several published values being $[\alpha]_D$ +225° in alcohol. The addition of chloroform, which enables a stronger solution to be made, raises the specific rotation (+234°). An *M*/40 solution in 0·1*N*-H_2SO_4 shows $[\alpha]_D^{15}$ +263·7°. Cinchonine is soluble in 3,810 parts of water at 10°, 3,670 at 20°, and 2,500 at 100°; it dissolves in 115 parts of alcohol at 17°, but in 28 parts of the boiling solvent; in 370 parts of cold ether (sp.gr. 0·73), and in 18 parts of a mixture of alcohol (4) and chloroform (1), although its solubility in chloroform alone is only about one-third of that in alcohol. Cinchonine is fairly soluble in boiling amyl alcohol and in hot, but not cold, benzene. The addition of alkalis to aqueous solutions of cinchonine salts produces an amorphous precipitate which gradually becomes crystalline, and which is stated to be more easily soluble in solvents than the crystalline form. Cinchonine begins to sublime at about 220° and boils with some decomposition above its melting-point; in a vacuum, however, it is volatile unchanged. It is non-fluorescent and does not give the thalleioquin reaction. Unlike cinchonidine, it forms a soluble tartrate. Like quinine, cinchonine is bitter to the taste. Although cinchonine is a fairly strong diacidic base, aqueous solutions of its salts are liable to hydrolyse and to deposit the base. On oxidation with potassium permanganate it gives rise to cinchotenine, and with chromic acid it furnishes cinchoninone, cinchoninic acid, meroquinene, cincholoiponic acid, and loiponic acid (for fuller descriptions of these products of oxidation, *see below*). On catalytic hydrogenation, hydrocinchonine (*q.v.*) is formed, while heating the acid sulphate with a little water at 140°, or boiling a solution of cinchonine in dilute acetic acid, gives rise to cinchotoxine (cinchonicine) (*see below*). With strong mineral acids various addition and transformation products are formed; and with amyl alcoholic potash cinchonine enters into dynamic equilibrium with *epi*cinchonine, *epi*cinchonidine, and cinchonidine.

Cinchonine Sulphate, $B_2 \cdot H_2SO_4,2H_2O$, crystallises from water in the form of hard, transparent prisms, which become anhydrous at 100°, and then have m.p. 200° (*decomp.*). It is readily soluble in alcohol, less so in water (70 parts cold, 13 parts at 100°), and dissolves in chloroform to about the same extent as in water (distinction from quinine and cinchonidine). The salt dissolves in 2,300 parts of ether at 25°. In 97% alcohol it shows $[a]_D$ +193·3°−0·374*c*, where c=grams of base in 100 c.c. The optical rotation in chloroform is +133°.

Cinchonine Acid Sulphate, $B \cdot H_2SO_4,4H_2O$, large, colourless prisms, is difficult to crystallise, being very soluble both in water and in alcohol.

Cinchonine Hydrochloride, $B \cdot HCl,2H_2O$, crystallises from water in efflorescent prismatic crystals, which contain only $1H_2O$ when dried in the air. The anhydrous salt melts at 217°–218° (*decomp.*) (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 819). It has $[a]_D^{20\cdot5}$ +177·4° (c=1·083 anhydrous salt in water) ; $[a]_D^{25}$ +133·6° (c=1·407 in chloroform); $[a]_D^{15}$ +165·5° (2·425*c* in water) +214° (1·72*c* in water containing 2 equivalents of HCl) +172·7° (*c*=1 in 97% alcohol), and +163·6° (*c*=10 in 97% alcohol). The salt is soluble in the cold in 22 parts of water, in 1 part of alcohol, and 290 parts of ether. It also dissolves in chloroform.

Among other salts of cinchonine may be mentioned the dihydrochloride, hydrobromide, dihydrobromide, hydriodide, dihydriodide, hydriodate, nitrate, oxalate, *d*-tartrate, and bitartrate, *l*-bitartrate, benzoate, two citrates, salicylate, succinate and thiocyanate. A number of double compounds with metallic salts are known.

Cinchonine Methiodide,

$$C_9H_6N—CH(OH)—C_7H_{11}N(CH_3I)—CH=CH_2,$$

is formed with a little difficulty from the components and melts at 254° (Claus and Müller, Ber. 1880, **13**, 2290, footnote).

Cinchonine Ethiodide,

$$C_9H_6N—CH(OH)—C_7H_{11}N(C_2H_5I)—CH=CH_2,$$

is prepared by the gradual addition of ethyl iodide to a boiling solution of cinchonine in alcohol in the dark. It crystallises from water in white, silky anhydrous needles, decomp. 260° (Claus and Kemperdick, Ber. 1880, **13**, 2286).

Isomeric *Cinchonine Ethiodide*,

$$C_9H_6N(C_2H_5I)—CH(OH)—C_7H_{11}N—CH=CH_2,$$

is made by heating 40 parts of cinchonine hydriodide with 15 parts of alcohol and 15 parts of ethyl iodide for 2 hours under pressure. The product (base) crystallises from water in orange needles, and from alcohol in orange prisms, m.p. 184° (*indef.*) (Skraup and von Norwall, Monatsh. 1894, **15**, 40). It is oxidised with potassium permanganate to the ethiodide of cinchoninic acid (Skraup, *ibid.* 433), and with a further molecule of ethyl iodide readily gives *cinchonine diethiodide*,

$$C_9H_6N(C_2H_5I)—CH(OH)—C_7H_{11}N(C_2H_5I)—CH=CH_2,$$

also formed from the white monoethiodide, or from cinchonine, by heating at 150° with ethyl iodide in a sealed tube. It crystallises from water in large, dark yellow prisms with $1H_2O$, *decomp.* 264°. It is readily soluble in water, and less soluble in alcohol than the white monoethiodide (Claus and Kemperdick, Ber. 1880, **13**, 2288).

Acetylcinchonine,

$$C_9H_6N—CH(O \cdot COCH_3)—C_7H_{11}N—CH=CH_2,$$

results from the action of acetic anhydride at 60°–80° for 2 hours. Amorphous powder (Hesse, Annalen, 1880, **205**, 321 ; Hilditch, J.C.S. 1911, **99**, 238 ; Seekles, Rec. trav. chim. 1923, **42**, 71).

Benzoylcinchonine,

$$C_9H_6N—CH(O—COC_6H_5)—C_7H_{11}N—CH=CH_2,$$

is prepared by the action of excess of benzoyl chloride on cinchonine. It crystallises in prisms from ether and melts at 106°–107° (Léger, Bull. Soc. chim. 1893, **9**, 714 ; *see also* Skraup, Monatsh. 1895, **16**, 163, and Seekles, Rec. trav. chim. 1923, **42**, 71).

a-Chlorohydrocinchonine, better *a*-chlorodihydrocinchonine (component of "hydrochlorocinchonine"),

$$C_9H_6N—CH(OH)—C_7H_{11}N—CHCl—CH_3,$$

is isolated as the dihydrochloride from the products of the reaction of concentrated hydrochloric acid and cinchonine (Goodson, J.C.S. 1935, 1096). The base crystallises from alcohol in needles, has m.p. 236° (*decomp.*) and $[a]_D^{20}$ +226·0° (c=0·5 in *N*-HCl). The dihydrochloride melts at 283°.

The mother-liquors from the crude dihydrochloride contain *α′-chlorohydrocinchonine*, which is epimeric with the α-derivative at the carbon atom carrying the chlorine atom. It is purified in the form of its tartrate, which is crystallised from methyl alcohol. The base, which crystallises from alcohol in minute needles, has m.p. 223° (*decomp.*), and $[\alpha]_D^{22}$ +176·0° (c=0·5 in N-HCl). The dihydrochloride melts at 276° (*decomp.*) and the tartrate, which crystallises from methyl alcohol with $2H_2O$ melts, when anhydrous, at 212° (*decomp.*).

Bromohydrocinchonine, better bromodihydrocinchonine (hydrobromocinchonine),

$$C_9H_6N{-}CH(OH){-}C_7H_{11}N{-}CHBr{-}CH_3,$$

first prepared from cinchonine by Skraup (Annalen, 1880, **201**, 324) and Comstock and Koenigs (Ber. 1887, **20**, 2520), is obtained from cinchonine or α- or β-*iso*cinchonine, *allo*cinchonine, or α- or β-hydroxyhydrocinchonine by heating with 10 parts of 50% hydrobromic acid at 100° (Skraup, Copony and Medanich, Monatsh. 1900, **21**, 512 ; Zwerger, *ibid.* 1903, **24**, 119 ; Léger, Bull. Soc. chim. 1918, [iv], **23**, 133, 328; 1919, [iv], **25**, 260). The base has m.p. 185°; the dihydrobromide crystallises from dilute hydrobromic acid in colourless prisms, m.p. 242°–243° (Zwerger), $[\alpha]_D^{17}$ +149·1° (c=1·989 in water) (Léger). The French author also mentions a stereoisomeric bromohydro-compound, $[\alpha]_D^{22}$ +127·3°.

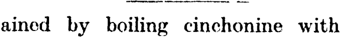
α-Iodohydrocinchonine (hydroiodocinchonine),

$$C_9H_6N{-}CH(OH){-}C_7H_{11}N{-}CHI{-}CH_3,$$

is formed in predominating proportion when cinchonine or α-*iso*cinchonine is heated at 100° with hydriodic acid (sp.gr. 1·7). The base, microscopic colourless leaflets, has m.p. 153°–156° (*decomp.*). The hydrochloride has $[\alpha]_D$ +189·2° (Léger, *ibid.*, 1918, [iv], **23**, 240).

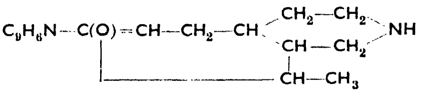
α′-Iodohydrocinchonine (hydroiodo*apo*cinchonine) is the epimeride of the preceding substance at the iodine-carbon atom, and is formed from *allo*cinchonine and β-*iso*cinchonine. Its hydrochloride has $[\alpha]_D$ +170·5° (Léger, *l.c.*).

α-iso*Cinchonine* (cinchoniline),



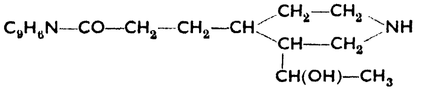
$$\underbrace{C_9H_6N{-}CH(O){-}C_7H_{11}N{-}CH}{-}CH_3,$$

is obtained by boiling cinchonine with four times its weight of 50% sulphuric acid (Jungfleisch and Léger, Compt. rend. 1887, **105**, 1255 ; 1888, **106**, 68, 657 ; 1891, **113**, 651 ; Ann. Chim. 1920, **14**, 62, 129 *et seq.* ; Hesse, Annalen, 1888, **243**, 147 ; 1890, **260**, 213). It can also be prepared in a variety of other ways, such as heating cinchonine with hydrochloric acid (Hesse, *ibid.* 1893, **276**, 91), or, best perhaps, by removal of hydrogen halide from halogenohydrocinchonine by means of alcoholic potash (Comstock and Koenigs, Ber. 1887, **20**, 2521 ; Skraup, Monatsh. 1891, **12**, 431 ; 1899, **20**, 585 ; Ber. 1892, **25**, 2909 ; Jungfleisch and Léger, Compt. rend. 1894, **118**, 29). The last method is to be preferred on account of yield, Hesse (Annalen, 1893, **276**, 95) having shown that α-*iso*cinchonine is converted into the β-isomeride by the action of sulphuric acid. α-*iso*Cinchonine is, nevertheless, characterised by its great stability (Rabe and Böttcher, Ber. 1917, **50**, 127) ; it can be distilled without decomposition. It crystallises from ether in colourless anhydrous prisms, m.p. 130·4°, $[\alpha]_D^{17}$ +53·1° (c=1 in 97% alcohol), and +62·6° in water containing 4 equivalents of HCl. It is almost insoluble in water, but dissolves readily in alcohol, ether, acetone, benzene or chloroform. It is a strong bitertiary base, which is alkaline even to phenolphthalein. Its oxygen atom has the ether function, for it cannot be acylated, and does not react with phenylhydrazine. The hydrochloride, $B{\cdot}HCl,3H_2O$, has m.p. 226°, and $[\alpha]_D^{16}$ +5° (c=1 of anhydrous salt in water). On heating its acid sulphate to 140°, α-*iso*cinchonine undergoes the " Pasteur " reaction (Skraup and Zwerger, Monatsh. 1900, **21**, 535 ; Kaas, *ibid.* 1905, **26**, 119) giving rise to " α-*iso*-ψ-cinchonicine," which, in the light of the researches of Suszko and his collaborators on the *iso*quinidines, must be formulated as



$$C_9H_6N{-}C(O){=}CH{-}CH_2{-}CH\begin{matrix}CH_2{-}CH_2\\CH{-}CH_2\end{matrix}NH \quad (C(O)\text{ linked to } CH{-}CH_3 \text{ on the } CH)$$

(*see* Dubas, Konopnicki and Suszko, Rocz. Chem. 1933, **13**, 464). On boiling with dilute acetic acid, α-*iso*cinchonine is converted into hydroxyhydrocinchotoxine,



$$C_9H_6N{-}CO{-}CH_2{-}CH_2{-}CH\begin{matrix}CH_2{-}CH_2\\CH{-}CH_2\\|\\CH(OH){-}CH_3\end{matrix}NH$$

(Rabe and Böttcher, *l.c.*).

β-iso*Cinchonine* (cinchonigine), a stereoisomeride of the preceding substance, is probably epimeric with it at carbon atom " 5 " (*see* section 5*d*, p. 149*c*) and is usually formed side by side with it, as well as from it by the action of sulphuric acid (*see* references above, and Jungfleisch and Léger, Compt. rend. 1888, **106**, 357 ; Ann. Chim. 1920, **14**, 105 *et seq.* ; Hesse, Annalen, 1893, **276**, 88 ; Skraup, Monatsh. 1899, **20**, 571 ; 1900, **21**, 512). It is even more stable than α-*iso*cinchonine. It exhibits dimorphism and separates from ether in transparent anhydrous crystals, belonging either to the orthorhombic or clinorhombic systems. The two forms are reversibly interconvertible. β-*iso*Cinchonine has m.p. 130·7°, $[\alpha]_D^{17}$ −60·1° (c=1 in 97% alcohol), and −36° in water containing 4 equivalents of HCl. It is almost insoluble in water, but readily soluble in most organic solvents including ether. It is a strong bitertiary base, but weaker than its α-isomeride, being alkaline to litmus, but not to phenolphthalein. It contains no hydroxyl or keto-group. The hydrochloride melts at 213°, and is soluble in about 50 parts of cold water ; $[\alpha]_D^{17}$ −65·2° (c=1, anhydrous salt, water). On heating its acid sulphate to 140° β-*iso*cinchonine, like the α-isomeride, undergoes the " Pasteur " reaction (Skraup, Copony, and Medanich, Monatsh. 1900, **21**, 512 ; Kaas, *ibid.* 1904, **25**, 1145 ; 1905, **26**, 119) giving rise to " β-*iso*-ψ-cinchonicine." The same substance is also obtained by the isomerisation of cinchotoxine (oxalate) by means of concentrated sulphuric acid at 100° (Skraup and Egerer, *ibid.* 1903, **24**, 669).

allo*Cinchonine* (*apo*cinchonine, *pseudo*cinchonine),

$$C_9H_6N—CH(OH)—C_6H_{10}N{>}C=CH—CH_3,$$

is an isomeride of the preceding two substances, and is usually formed along with them. It is a bitertiary base, forms acyl derivatives and adds the elements of hydrogen halide, giving rise to a small proportion of the same substances, which, under like conditions, are formed from cinchonine : the greater proportion of the resulting halogen derivatives are the same as those produced from β-*iso*cinchonine. It crystallises from alcohol, has m.p. 216°–218° and $[\alpha]_D^{18}$ $+150°$ ($c=1$ in alcohol). It is characterised by the sparing solubility of the base in ether, and of the neutral sulphate in water (Jungfleisch and Léger, Ann. Chim. 1920, **14**, 145 *et seq.*, in which are further references to *allo*cinchonine). Although a geometrical isomeride of *allo*cinchonine is unknown, a base, m.p. 232°–234°, not identified with certainty, by Jungfleisch and Léger (*ibid.* 181), probably constitutes the missing substance.

α-*Hydroxyhydrocinchonine*, better α-hydroxydihydrocinchonine,

$$C_9H_6N—CH(OH)—C_7H_{11}N—CH(OH)—CH_3,$$

is formed together with the preceding substances when cinchonine is heated with 50% sulphuric acid (Jungfleisch and Léger, Compt. rend. 1887, **105**, 1255 ; 1888, **106**, 68 ; 1889, **108**, 952 ; Ann. Chim. 1920, **14**, 71 *et seq.*; Léger, Compt. rend. 1918, **166**, 903 ; 1919, **168**, 404). It crystallises in colourless prisms, m.p. 252° (*decomp.*), $[\alpha]_D^{18}$ $+182{\cdot}6°$ ($c=1$ in 97% alcohol). It is characterised by its sparing solubility in ether and ready solubility in 50% alcohol. It is almost insoluble in water, but dissolves readily in acetone, benzene or chloroform. α-Hydroxyhydrocinchonine gives rise to a diacetyl derivative. It is a strong bitertiary base alkaline to phenolphthalein. The neutral hydrochloride, $B{\cdot}HCl,H_2O$, has m.p. 230° and $[\alpha]_D^{13}$ $+174{\cdot}4°$ ($c=1$ in water with 1 equivalent of HCl). The salt is very sparingly soluble in water.

β-*Hydroxyhydrocinchonine*, better β-hydroxydihydrocinchonine, is the epimeride of the foregoing substance at carbon atom " 5 " (*see* section 5*d*, p. 149*c*). The two epimerides are formed together (*see* references above, and Jungfleisch and Léger, Compt. rend. 1894, **119**, 1268; 1919, **168**, 404 ; Ann. Chim. 1920, **14**, 89 *et seq.*). It crystallises from 90% alcohol in small, colourless, prismatic needles, m.p. 273° (*decomp.*), $[\alpha]_D^{18}$ $+187{\cdot}2°$ ($c=1$ in 97% alcohol), or $+203{\cdot}1°$ in water containing 2 equivalents of HCl. Although it is insoluble in water, β-hydroxyhydrocinchonine is not immediately precipitated by alkalis from aqueous solutions of its salts, but separates in a fine mass of needles after some hours. It is readily soluble in alcohol, but not in acetone. It has a low solubility in chloroform, although this solvent will take up a good deal of the base at the moment of precipitation from its salts ; the greater part of the alkaloid is soon deposited in the crystalline state. Like the α-epimeride it forms a diacetyl derivative, and is alkaline to phenolphthalein. A number of salts have been described.

α- and β-*Cinchonhydrine*, components of " δ-cinchonine," are substances of disputed constitution, the formulæ in question being $C_{18}H_{22}ON_2$, $C_{19}H_{24}ON_2$, and $C_{19}H_{22}ON_2$. They are formed together with the cinchonine isomerides described above, when bromohydrocinchonine base is heated with dilute alcohol, or with alcoholic potash (Jungfleisch and Léger, Compt. rend. 1894, **118**, 29 ; Ann. Chim. 1920, **14**, 158, 162, 165 ; Léger, Compt. rend. 1919, **169**, 797 ; Cordier von Löwenhaupt, Monatsh. 1898, **19**, 472 ; von Arlt, *ibid.* 1899, **20**, 440 ; Langer, *ibid.* 1901, **22**, 157). The α-isomeride crystallises from ether in prisms, m.p. 144·4°, $[\alpha]_D^{19}$ $+195{\cdot}8°$ ($c=1$ in water containing 2 equivalents of HCl), or $+139{\cdot}8°$ in alcohol. The β-isomeride is similar. It crystallises from ether in prismatic needles, m.p. 155·8°, $[\alpha]_D^{21}$ $+106°$ ($c=1$ in water containing 2 equivalents of HCl), or $+72{\cdot}2°$ in alcohol. The cinchonhydrines are said to be the analogues of niquine (*see under* QUININE), and to be tertiary-secondary bases ; they form diacetyl-derivatives.

A number of other " transformation products " of cinchonine are described in the literature. Most of these, if not all, can be ignored ; some are identical with, or are impure forms of, one or other of the substances described above ; many are obvious mixtures of one or more of the authentic compounds with one another, or with hydrocinchonine (derived from commercial cinchonine). For a valuable summary of the position in 1899, which is still largely valid owing to the fact that most of these spurious isomerides had been prepared before that time, *see* Skraup, Monatsh. 1899, **20**, 571.

Cinchotoxine (cinchonicine),

$$C_9H_6N—CO—CH_2—CH_2—C_5H_9N—CH=CH_2,$$

occurs in commercial quinoidine, the question of its pre-existence in the bark being in dispute. It is best obtained artificially from cinchonine or cinchonidine, either by melting (or heating with glycerol at 210°) the acid sulphate or tartrate, of either base, or, best perhaps, by the " wet " process of von Miller and Rohde (Ber. 1895, **28**, 1064), in which cinchonine is boiled with 14 parts of 7% acetic acid for 33 hours. Cinchotoxine crystallises from absolute ether at 0° in long, thin prisms, m.p. 58°–59°, $[\alpha]_D$ $+46{\cdot}5°$ in chloroform ($c=2$), $+47{\cdot}2°$ (Howard and Chick, *v. infra*), and $+57{\cdot}7°$ (Roques, *v. infra*), in alcohol; $+35{\cdot}6°$ ($c=1$ in water containing 4 equivalents of HCl). It is readily soluble in ether (2 parts), alcohol, benzene or chloroform, less so in petroleum ; it dissolves in 564 parts of water at 18°, but is more soluble in aqueous solutions of ammonium salts, from which it expels ammonia ; it is a strong base which absorbs carbon dioxide from the air. Cinchotoxine forms a crystalline hydriodide, oxalate, tartrate, nitrate (m.p. 160°), and double salts with zinc, cadmium, and platinic chlorides. Cinchotoxine is a tertiary-secondary base, which forms crystalline alkylhalides. It is a ketone, forming a yellow phenylhydrazone, m.p. 148°, from a mixture of alcohol and light petroleum. Cinchotoxine is non-fluorescent and does not respond to the thalleioquin reaction, but gives a magnificent purple coloration with diazobenzenesulphonic acid in presence of alkali. It reacts with amyl nitrite in presence of sodium ethoxide to form an *iso*nitroso- derivative, and with nitrous acid gives a nitrosamine (**N**-nitroso-derivative). (*See* Pasteur, Compt. rend. 1853, **37**, 110; Hesse, Annalen, 1868, **147**, 241; 1873, **166**, 277; 1875, **178**, 253; Howard, J.C.S. 1872, **25**, 101; Howard and Chick, J.S.C.I. 1909, **28**, 55; Roques, Bull. Soc. chim. 1895, [iii], **13**, 1005; Ann. Chim. 1897, **10**, 234).

epi*Cinchonine*, $C_{19}H_{22}ON_2$, is epimeric with cinchonine about the carbinol ($CH{\cdot}OH$) group. It is obtained by reducing cinchoninone (100 g.), dissolved in a solution of sodium ethoxide (**Na** 84 g. in alcohol 2,280 c.c.), with aluminium powder (84 g.). The *epi*cinchonine is isolated from the ether-soluble fraction of the stereoisomerides formed, with the aid of tartaric, dibenzoyl-, and dianisoyl- tartaric acids. It crystallises from ether in long, colourless prisms, pointed at their ends, m.p. 82°–83°, $[\alpha]_D^{22}$ +120·3° (c= 0·8064 in alcohol). It is non-fluorescent, and very soluble in all the usual organic solvents (Rabe and others, Annalen, 1932, **492**, 253).

Cinchoninone,

$$C_9H_6N{-}CO{-}C_7H_{11}N{-}CH{=}CH_2,$$

is obtained in very low yield by the gentle oxidation of cinchonine or cinchonidine with chromic acid (Rabe, Ber. 1907, **40**, 3655; 1908, **41**, 62; Annalen, 1909, **364**, 338). It is best prepared indirectly from cinchotoxine. The toxine (58 g.) in cold N-hydrochloric acid (200 c.c.), covered with a layer of ether and well stirred, is first **N**-brominated by introducing in a thin stream a cold solution of bromine (32 g.) in 6% sodium hydroxide solution (400 g.) (*i.e.* $NaOBr$). The **N**-bromotoxine (m.p. 153°) crystallises from ether, and is converted to cinchoninone by treating a hot solution of 1 g. in 25 c.c. of alcohol with 3 c.c. of a cold sodium ethoxide solution containing **Na** 0·15 g. (Rabe, Ber. 1911, **44**, 2089). Cinchoninone crystallises from ether or from 50% alcohol in well-defined, faintly yellow prisms, m.p. 126°–127°. It exhibits mutarotation, the final values being $[\alpha]_D^{20}$ +76·1° (c=3·302 in 99% alcohol), and $[\alpha]_D^{14}$ +74·7° (c=3·305 in benzene) (Rabe and others, Annalen, 1910, **373**, 110). Cinchoninone is readily soluble in alcohol, ether, benzene or chloroform, but not in water, and sparingly soluble in light petroleum. It dissolves slightly with a yellow colour in aqueous alkalis (enolisation). The hydrochloride (m.p. 252°–253°) is very soluble in water. The initial values of the optical rotation of this salt depend on whether it has been prepared from a fresh or stale solution of the base; the final values, however, are the same: $[\alpha]_D^{14}$ +166·6° (c=1·656 in chloroform) and +66·4° in water (Rabe and others, *l.c.*). Cinchoninone forms an amorphous oxime, and a benzoyl-derivative (derived from the enol-form), which crystallises from petroleum (b.p. over 80°) in white needles, m.p. 133°. On reduction in a suitable manner, cinchoninone gives rise to cinchonine, *epi*cinchonine, *epi*cinchonidine, and cinchonidine.

Cinchonine Chloride,

$$C_9H_6N{-}CHCl{-}C_7H_{11}N{-}CH{=}CH_2,$$

is prepared by treating dry cinchonine hydrochloride (33 g.) in chloroform (300 c.c.) with phosphorus pentachloride (50 g.) in the cold (Rabe and others, Annalen, 1910, **373**, 101). The product (m.p. 72°) crystallises from ether or from aqueous alcohol with $2H_2O$, which is lost over sulphuric acid: the anhydrous base then melts at 110°, and has $[\alpha]_D^{13}$ +55·7° (c=1·975 in 99% alcohol), and +62·2° (c=2·007 in chloroform). It is readily soluble in most organic solvents, but not in water (Koenigs, Ber. 1880, **13**, 286). Its hydrochloride has $[\alpha]_D^{24}$ +49·5° (c=1·5555 in water).

Desoxycinchonine,

$$C_9H_6N{-}CH_2{-}C_7H_{11}N{-}CH{=}CH_2,$$

is made by reducing cinchonine chloride dissolved in 20 parts of 10% sulphuric acid, with 1½ parts of iron filings at room temperature for 72 hours. The desoxy-base crystallises from light petroleum, has m.p. 91°, and $[\alpha]_D^{13}$ +179·3° (c=2·025 in 99% alcohol), and +194·3° in chloroform (Rabe and others, Annalen, 1910, **373**, 105, 106).

Cinchene,

$$C_9H_6N{-}CH{=}C{<}C_6H_{10}N{-}CH{=}CH_2,$$

is formed when cinchonine or cinchonidine chloride is boiled with alcoholic potash. It crystallises from light petroleum in colourless leaflets, m.p. 123°–125°, and is dextrorotatory. It can be distilled without decomposition (Koenigs, Ber. 1881, **14**, 1854; Koenigs and Comstock, *ibid.* 1885, **18**, 1219; Koenigs, *ibid.* 1895, **28**, 3146).

apo*Cinchene*, 4-(6-hydroxy-3:4-diethylphenyl)-quinoline,

$$C_9H_6N{-}C_6H_2(OH)(C_2H_5)_2$$

(Kenner and Statham, J.C.S. 1935, 299), is obtained by heating cinchene with hydrobromic acid (sp.gr. 1·49) at 180° under pressure for 6 to 8 hours (Koenigs, Ber. 1881, **14**, 1854; Koenigs and Comstock, *ibid.* 1885, **18**, 1226). It crystallises from alcohol, and melts at 209°–210°. Salts and ethers of *apo*cinchene are known (*see* Comstock and Koenigs, *ibid.* 1885, **18**, 2379; 1887, **20**, 2674; Koenigs, J. pr. Chem. 1900, [ii], **61**, 1).

Cinchoninal,

$$C_9H_6N{-}CH(OH){-}C_7H_{11}N{-}CH{=}O,$$

and its acyl (acetyl and benzoyl) derivatives,

$$C_9H_6N{-}CH(O{-}COR){-}C_7H_{11}N{-}CH{=}O,$$

are obtained from cinchonine and from its acyl derivatives by the action of ozone in cold chloroform solution. The resulting ozonides furnish on hydrolysis [formaldehyde], hydrogen peroxide, and the aldehydic substances in question. The latter are amorphous. Cinchoninal has $[\alpha]_D$ +100·5° in chloroform; the acetyl-derivative has $[\alpha]_D$ +28·2°, and the benzoyl-derivative −72·4° (Seekles, Rec. trav. chim. 1923, **42**, 69).

Cinchotenine,

$C_9H_6N{-}CH(OH){-}C_7H_{11}N{-}CO_2H$,

is obtained by oxidising a cooled solution of cinchonine in dilute sulphuric acid with potassium permanganate. It crystallises from water with $3H_2O$, m.p. 197°–198°, $[\alpha]_D^{15}$ +115·5° ($c=2$ of trihydrate in a mixture of 2 vols. chloroform and 1 vol. alcohol), +175·5° in dilute sulphuric acid (Hesse, Annalen, 1875, **176**, 233; Skraup, *ibid.* 1879, **197**, 379). Cinchotenine is soluble in hot water, but sparingly in alcohol. It dissolves readily in dilute acids and caustic alkalis, and is precipitated from the latter by carbon dioxide. As an acid, cinchotenine forms salts, esters and an acid chloride. Like cinchonine it can be acylated, but does not react with the halogens or with their hydracids. It is stable to cold permanganate, but is rapidly oxidised by the hot reagent. With chromic acid the same oxidation products (but no meroquinene) result as in the like oxidation of cinchonine.

Cinchoninic Acid, quinoline-4-carboxylic acid, $C_9H_6N{-}COOH$, was first made by Caventou and Willm (Bull. Soc. chim. 1869, [ii], **12**, 214) by the oxidation of cinchonine with potassium permanganate. It is the most readily isolated of the oxidation products of cinchonine, cinchonidine, their hydro- derivatives, and many of the derivatives and degradation products of these. It can be prepared by the oxidation of cinchonine with chromic acid (Koenigs, Ber. 1879, **12**, 97) or nitric acid (Claus and Muchall, *ibid.* 1885, **18**, 362) or by oxidation with nitric acid of the condensation product of lepidine with formaldehyde. It has been synthesised by the interaction of isatin with acetaldoxime under the agency of 40% potassium hydroxide (Pfitzinger, J. pr. Chem. 1902, [ii], **66**, 263; *cf.* Kaufmann, and Peyer, Ber. 1912, **45**, 1805; Thielepape, *ibid.* 1938, **71**, 387). Cinchoninic acid crystallises from water in needles with $1H_2O$, or in prisms with $2H_2O$, depending on the conditions, and becomes anhydrous at 100°. It has m.p 253°–254°, is insoluble in ether, and sparingly soluble in water and in alcohol.

Lepidine, 4-methylquinoline, $C_9H_6N{-}CH_3$, was first isolated from the products of dry distillation of cinchonine with potash (Greville Williams, 1855), and has been synthesised by heating on the water-bath a mixture of equimolecular parts of aniline, acetone, and methylal (or formaldehyde) saturated with hydrogen chloride (C. Beyer, J. pr. Chem. 1886, [ii], **33**, 418). Lepidine can be prepared by heating hydrocinchene or cinchene with 25% phosphoric acid at 170°–180° (Koenigs, Ber. 1894, **27**, 1501; 1890, **23**, 2677). Lepidine is a hygroscopic, sternutatory oil, b.p. 264·2°/760 mm., which solidifies on cooling and then melts at 9°–10°. It is sparingly soluble in water and is volatile in steam.

Oximinovinylquinuclidine, vinylquinuclidone-oxime, $HO{-}N{=}C{<}C_6H_{10}N{-}CH{=}CH_2$, is formed together with cinchoninic acid from cinchoninone (or with quininic acid from quininone), when these ketones, dissolved in cold alcoholic sodium ethoxide, are treated with a little more than one molecular proportion of amyl nitrite. It crystallises from a mixture of ether and light petroleum (b.p. 40°) in white needles, or from ethyl acetate in colourless prisms, m.p. 146°–147°. The oxime is readily soluble in water, alcohol and benzene, fairly soluble in ether and ethyl acetate, and sparingly soluble in light petroleum. It is volatile in steam, and sublimes below its melting-point. On hydrolysis with hydrochloric acid, the bicyclic system undergoes rupture, and there are formed hydroxylamine and meroquinene (Rabe, Ber. 1908, **41**, 68; Annalen, 1909, **365**, 361).

Meroquinene, 3-vinylpiperidine-4-acetic acid,

$CH_2{=}CH{-}C_5H_9N{-}CH_2{-}CO_2H$,

is present among the products of oxidation of cinchonine, cinchotoxine, and quinine with chromic acid (Koenigs, Ber. 1894, **27**, 1501; Annalen, 1906, **347**, 196, 198). It is readily prepared by heating cinchene or quinene with 25% phosphoric acid at 170°–180° (Koenigs, Ber. 1894, **27**, 901, 904; Annalen, 1906, **347**, 194, 195). Its N-methyl derivative is very readily obtained by subjecting *iso*nitroso-N-methylcinchotoxine to the Beckmann rearrangement, when the easily isolable N-methylmeroquinene-nitrile is formed (Rabe and Ritter, Ber. 1905, **38**, 2770). From a mixture of methyl alcohol and ethyl acetate meroquinene separates in almost colourless crystals, m.p. 223°–224°, $[\alpha]_D^{20}$ +27·6° ($c=10$ in water). It is very soluble in water, very sparingly so in cold alcohol, and almost insoluble in ether or chloroform. Its hydrochloride has m.p 146°–148°, and the N-nitroso-derivative melts at 67°. On reduction with zinc and hydriodic acid, meroquinene is converted to cincholoipon (*see under* Hydrocinchonine, *below*) (Koenigs, Ber. 1902, **35**, 1350), and on oxidation with cold potassium permanganate in acid solution it gives rise to Skraup's cincholoiponic acid. Meroquinene is an amphoteric substance; its ethyl ester is a strong monoacidic base, while its N-acetyl and -nitroso- derivatives are monobasic acids.

d-*β-Cincholoiponic Acid,* 3-carboxypiperidine-4-acetic acid, $HO_2C{-}C_5H_9N{-}CH_2{-}CO_2H$, results from the oxidation either with potassium permanganate or chromic acid or both, of all the vinyl-alkaloids, of the toxines and tenines, of meroquinene, of cincholoipon, and of numerous other transformation and degradation products of the cinchona alkaloids (Skraup, Monatsh. 1888, **9**, 783; 1889, **10**, 39; 1895, **16**, 175; 1896, **17**, 365; with Würstl, *ibid.* 1899, **10**, 225; with Pum, *ibid.* 227; Schniderschitsch, *ibid.* 1889, **10**, 54, 57; Würstl, *ibid.* 67, 70; Koenigs, Ber. 1895, **28**, 3150; Annalen, 1906, **347**, 208). It has been synthesised by Wohl, Losanitsch and Maag (Ber. 1907, **40**, 4698; 1909, **42**, 627). Cincholoiponic acid crystallises from water in prisms containing $1H_2O$ (m.p. 126°–127°) which is lost at 120°–125°. The anhydrous acid melts at 225°–226°, and has $[\alpha]_D^{20}$ +30·1° ($c=4$ in water). It is very soluble in water and readily so in alcoholic hydrogen chloride, but it is insoluble in absolute alcohol and in ether. Its hydrochloride has m.p. 192°–194°, $[\alpha]_D^{20}$ +38° ($c=4$ in water), and is fairly soluble in cold water and in alcohol, more sparingly so in hydrochloric acid. Cincholoiponic acid behaves as a monobasic acid, but its N-nitroso- and N-acetyl derivatives manifest full dibasic properties. On oxidation with cold potassium permanganate solution it gives rise to loiponic acid.

Loiponic Acid, piperidine-3:4-dicarboxylic acid, $C_5H_9N(CO_2H)_2$, is obtained as described above (Skraup, Monatsh. 1896, **17**, 376). It is also found in small amount in the mother-liquors from the cincholoiponic acid obtained by the oxidation of cinchonine. Loiponic acid crystallises from water in prisms, m.p. 259°–260°. It is sparingly soluble in cold water, and dissolves in about 20 parts of hot water; it is almost insoluble in hot alcohol, readily soluble both in acids and in alkalis, and, on titration, behaves as a monobasic acid. It forms a nitroso-derivative, m.p. 167°–168°, and its hydrochloride (m.p. 216°–220°) has $[\alpha]_D$ about +12° (c=8·33 in water) (Koenigs, Ber. 1897, **30**, 1330).

Cinchotine. *See* Hydrocinchonine, p. 162*d*.

Cinchotoxine. *See under* Cinchonine, p. 157*c*.

Conchairamidine, $C_{22}H_{26}O_4N_2$, occurs in the bark of *Remijia Purdieana* together with cinchonine, cinchonamine, concusconine, chairamine, chairamidine, and conchairamine. It was isolated by Hesse (Annalen, 1884, **225**, 256). For a scheme of separation the original paper should be consulted (*ibid.* 211, 218). It is obtained as a crystalline sulphate from the filtrate remaining after the chairamine has been separated as hydrochloride, and the conchairamine as thiocyanate. Conchairamidine separates from its solutions as an oil, and this gradually crystallises with $1H_2O$. The anhydrous base has m.p. 114°–115°, and $[\alpha]_D^{15}$ −60° (c=3 in 97% alcohol). It is very soluble in alcohol, ether, chloroform, benzene, or acetone. It is a weak base, neutral to litmus. Concentrated sulphuric acid gives a dark green colour. The hydrochloride, $B{\cdot}HCl,3H_2O$, sulphate, $B_2{\cdot}H_2SO_4,14H_2O$, and other crystalline salts have been described.

Conchairamine, $C_{22}H_{26}O_4N_2$, was isolated by Hesse (Annalen, 1884, **225**, 246) from the mixture of alkaloids occurring in the bark of *Remijia Purdieana*. After removing concusconine as sulphate, and chairamine as hydrochloride, the conchairamine is precipitated by potassium thiocyanate. The base crystallises from alcohol in thick, colourless prisms, $B{\cdot}H_2O{\cdot}C_2H_5OH$, m.p. 82°–86°. The alcohol of crystallisation is expelled at 100°, leaving the monohydrate (m.p. 108°–110°) which, in its turn, becomes anhydrous and amorphous at 115°. The anhydrous form melts at about 120°, and has $[\alpha]_D^{15}$ +68·4° (c=2 in 97% alcohol). An acetic acid solution of conchairamine, precipitated with ammonia, yields white crystalline flocks of the base, which contain $1H_2O$, and dehydrate and melt at 110°. It is soluble in chloroform, ether, and hot alcohol. A solution in acetic acid gives a dark green coloration with concentrated nitric acid, and sulphuric acid produces a brown solution turning dark green. The base is neutral to litmus, but forms well-defined crystalline salts, such as the hydrochloride, $B{\cdot}HCl$, and sulphate, $B_2{\cdot}H_2SO_4{\cdot}9H_2O$. It forms two methiodides: one crystallises with $3H_2O$ and is white; the other, yellow, has $1H_2O$.

Concusconine, $C_{23}H_{26}O_4N_2$, was isolated as the sulphate by Hesse (Annalen, 1884, **225**, 234) from the alkaloids in the bark of *Remijia Purdieana*. The base crystallises from alcohol in monoclinic needles containing $1H_2O$, m.p. 144°; on further heating the melt solidifies, and re-melts at 206°–208°, $[\alpha]_D^{15}$ +40·8° (c=2 of the hydrate in 97% alcohol), but Howard and Chick (J.S.C.I. 1909, **28**, 55) record the value +19·57°. Concusconine is insoluble in water, very sparingly soluble in cold alcohol, and readily soluble in ether or chloroform. A solution in acetic or hydrochloric acid gives a dark green colour with concentrated nitric acid. With concentrated sulphuric acid a bluish-green colour is produced, turning to olive-green on warming. Concusconine is a weak base, neutral to litmus, and its salts are for the most part amorphous. It gives rise to two methiodides, and contains two methoxyl groups.

Conquinamine, $C_{19}H_{24}O_2N_2$, is present together with quinamine in small quantity in most cinchona barks, and was first isolated by Hesse (Ber. 1877, **10**, 2158). It is found in the alcoholic mother-liquors from which quinamine has been crystallised, and is isolated by means of light petroleum, and purified by crystallisation of the nitrate, oxalate, or hydrobromide. It crystallises from alcohol in long prisms or pyramids, m.p. 123°, $[\alpha]_D^{15}$ +204·4° (c=1 in alcohol). It is fairly soluble in alcohol, ether, or benzene, but not in 50% alcohol or in water. It resembles quinamine in behaviour, and seems to be closely related to it, for on melting its oxalate, or on heating with hydrochloric acid (sp.gr. 1·125) quinamicine and *apo*quinamine are formed, which are also obtained from quinamine. A number of crystalline salts of conquinamine have been described (Hesse, Annalen, 1881, **209**, 62; Oudemans, *ibid.* 38).

Conquinine. *See* Quinidine (p. 169*b*).

Cupreine, $C_{19}H_{22}O_2N_2$, occurs together with other cinchona alkaloids (but not cinchonidine) in the so-called "Cuprea bark" (*Remijia pedunculata*), which is no longer collected commercially, and there being no known way of preparing it artificially from other alkaloids, cupreine is now unobtainable. It was first isolated by Paul and Cownley (Pharm. J. 1884, **15**, 221, 401) from "*homo*quinine," a loose compound of quinine and cupreine, at first mistaken for a new alkaloid resembling quinine; *homo*quinine is claimed to have been discovered by Hesse's assistant, Tod (*see* Hesse, Ber. 1882, **15**, 857; 1883, **16**, 60), but it was first described in the published literature by Paul and Cownley (Pharm. J. 1881, **12**, 497). The name "*ultra*quinine" was proposed for it by Whiffen (*ibid.* 497) and "*homo*quinine" by Howard and Hodgkin (*ibid.* 528; J.C.S. 1882, **41**, 66); *see also* Hesse (Annalen, 1884, **225**, 95; 1884, **226**, 240; 1885, **230**, 55).

Cupreine crystallises from ether in concentrically grouped prisms containing $2H_2O$, which can only be expelled at 120°–125°. From dilute alcohol it crystallises with $1/3H_2O$.

The anhydrous base melts at 198° and has $[\alpha]_D^{17}$ $-175{\cdot}5°$ ($c=1{\cdot}2$ in alcohol). For rotations in various alkaline solutions, *see* Oudemans (Rec. trav. chim. 1890, **9**, 171). It is readily soluble in alcohol, but sparingly so in ether, chloroform, or benzene. As a phenol, cupreine dissolves freely in aqueous caustic alkalis, from which it is reprecipitated by carbon dioxide, but is not readily soluble in ammonia. Cupreine is non-fluorescent, but gives the thalleioquin reaction, and a red-brown coloration with ferric chloride solution. Stereochemically, cupreine is cinchonidine with a hydroxyl group in the 6-position of the quinoline nucleus, or the phenol of which quinine is the methyl ether, for cupreine gives rise to quinine when heated with 1½ molecules of methyl nitrate in presence of sodium methoxide in a sealed tube at 100° (Grimaux and Arnaud, Compt. rend. 1891, **112**, 774). With methyl iodide there are formed cupreine methiodide, dimethiodide, quinine methiodide or dimethiodide, depending on the conditions. With hydrochloric acid it gives rise, like quinine, to "*apo*quinine" (*see under* Quinine) (Hesse), and on catalytic hydrogenation to hydrocupreine (*see under* Hydroquinine) (Giemsa and Halberkann, Ber. 1918, **51**, 1325). It forms a diacetyl derivative.

The salts of cupreine are colourless, and the acid salts afford colourless solutions, but the neutral salts dissolve in water with an intense yellow colour. The *sulphate*, $B_2{\cdot}H_2SO_4$, crystallises from water in anhydrous needles (Howard and Chick, J.S.C.I. 1909, **28**, 55), m.p. 257° (*decomp.*) (Giemsa and Halberkann, *l.c.*), soluble in 813 parts of water at 17°, and in 209 parts at 100°. It is also sparingly soluble in alcohol. The *acid sulphate*, $B{\cdot}H_2SO_4$, contains $1H_2O$ according to Hesse, and Howard and Chick, but $2H_2O$ according to Oudemans (Rec. trav. chim. 1889, **8**, 147) and Giemsa and Halberkann. It separates in large, transparent, faintly yellow, prismatic plates, $[\alpha]_D^{22}$ $-197{\cdot}9°$ ($c=1{\cdot}1824$ in water), and is soluble in about 70 parts of cold water. A *tetrasulphate* is also known. *Cupreine hydrochloride*, $B{\cdot}HCl,H_2O$ (colourless needles), dissolves in about 50 parts of cold water, and has $[\alpha]_D^{17}$ $-154{\cdot}8°$ to $-157{\cdot}1°$ in water ($c=0{\cdot}57$ to $0{\cdot}86$), and $-167{\cdot}3°$ to $-169{\cdot}7°$ in alcohol ($c=0{\cdot}9$ to $1{\cdot}42$). For other salts the papers of Hesse and of Oudemans already cited should be consulted, and for physiological action of cupreine *see* Grimaux and Laborde (Compt. rend. Soc. Biol. 1892, **44**, 608).

The procedure whereby Grimaux and Arnaud (*l.c.*) succeeded in methylating cupreine to quinine enabled them also to prepare the following series of homologues of quinine :

Quinethyline, $C_{21}H_{26}O_2N_2$, ethylcupreine, (Compt. rend. 1891, **112**, 1364), m.p. 160° (*dry*), $[\alpha]_D$ $-169{\cdot}4°$. The sulphate, $B_2{\cdot}H_2SO_4,H_2O$, dissolves in 397 parts of water at 15°. According to Giemsa and Halberkann (Ber. 1918, **51**, 1332) the base has m.p. 165°–166°, and $[\alpha]_D^{20}$ $-158{\cdot}9°$ in alcohol.

Quinpropyline, $C_{22}H_{28}O_2N_2$, *n*-propylcupreine (Grimaux and Arnaud, Compt. rend. 1892, **114**, 672), m.p. 164° (*dry*). The sulphate, $B_2{\cdot}H_2SO_4,1\frac{1}{2}H_2O$, is soluble in 454 parts of water at 13°.

Quinisopropyline, $C_{22}H_{28}O_2N_2$, *iso*propylcupreine (*ibid.*), m.p. 154° ; $B_2{\cdot}H_2SO_4,H_2O$, dissolves in 367 parts of water at 10°.

Quinisoamyline, $C_{24}H_{32}O_2N_2$, *iso*amylcupreine (*ibid.*), is amorphous, m.p. 167°. $B_2{\cdot}H_2SO_4$ is soluble in 4,170 parts of water at 11·5°.

Unlike cupreine, the above homologous ethers fluoresce in dilute sulphuric acid solution. They are said to be more powerfully antipyretic, but more toxic than quinine (Grimaux, Laborde and Bourru, Compt. rend. 1894, **118**, 1303).

Cuscamidine, of undetermined composition, occurs in Cusco bark (*Cinchona Pelletierana*). It is amorphous, and is obtained together with cuscamine (which it closely resembles) by the addition of nitric acid to an acetic acid solution of the total alkaloids of the bark. The two bases are separated from one another as oxalates. The salts of cuscamidine are amorphous and are more soluble than those of cuscamine (Hesse, Annalen, 1880, **200**, 304).

Cuscamine, of undetermined composition, is obtained from Cusco bark (*see under* Cuscamidine, *above*). It crystallises from alcohol in prisms, m.p. 218°, is readily soluble in ether and in hot alcohol, but sparingly so in cold alcohol. It gives a yellow colour with concentrated sulphuric acid, turning brown on warming ; on adding molybdic acid a bluish-green colour is obtained, turning brown on heating, and violet-brown on re-cooling. With nitric acid a yellow coloration is obtained. Cuscamine is not a strong base, but many salts are known, some of which are crystalline (Hesse).

Cusconidine, of undetermined composition, is an amorphous alkaloid occurring in Cusco bark (*Cinchona Pelletierana*). It is obtained from cusconine mother-liquors (*see below*). Its salts are amorphous (Hesse, Annalen, 1880, **200**, 303).

Cusconine, $C_{23}H_{26}O_4N_2$, occurs in Cusco bark and is obtained as sulphate after removing the aricine (*q.v.*) as acetate. It was discovered by Leverkoehn in 1829. It crystallises from ether in white leaflets with $2H_2O$. The water is lost at 100° and the dry base has m.p. 110°, $[\alpha]_D^{15}$ $-54{\cdot}3°$ ($c=2$ in 97% alcohol). It dissolves in 35 parts of ether at 15°, more easily in alcohol or acetone, very readily in chloroform, and is insoluble in water. Cusconine gives the same colour reactions with sulphuric acid and with ammonium molybdate as does aricine (*q.v.*). It is a weak base : its salts have an acid reaction, and are amorphous (Hesse, Annalen, 1877, **185**, 296).

Dicinchonine (dicinchonicine), $C_{38}H_{44}O_2N_4$, has the same empirical composition as cinchonine, and although its molecular weight is half that indicated by the formula, Hesse prefers the double formula by analogy with diconquinine. It occurs in *Cinchona rosulenta* and in *C. succirubra* together with the other principal cinchona alkaloids. Being soluble and amorphous it tends to pass into the so-called "quinodine " fraction in quinine manufacture, and is recovered therefrom as the thiocyanate. It is purified by crystallisation of the hydrochloride. The free base is a yellow amorphous substance, m.p. 40°, $[\alpha]_D^{15}$ +91·7° (c=1·52 in 97% alcohol). It is very soluble in alcohol, ether, acetone, chloroform, or benzene, but not in alkalis. It does not give the thalleioquin reaction. It is a strong base, and its *hydrochloride*, $B\cdot 2HCl$, crystallises well (Hesse, Annalen, 1885, **227**, 153). On heating with hydrochloric acid, it is converted into the isomeric, amorphous di*apo*cinchonine, soluble in ether, alcohol, or chloroform, $[\alpha]_D$ +20° in alcohol (Hesse, Annalen, 1880, **205**, 333). Di*apo*cinchonine is a mixture of isomerides containing α- and β-*iso*cinchonine (Jungfleisch and Léger, Compt. rend. 1892, **114**, 1192; Hesse, Annalen, 1893, **276**, 118).

Diconquinine (diquinicine), $C_{40}H_{46}O_3N_4$, the essential constituent of commercial "quinoidine" (*q.v.*), is prepared by removing from quinoidine the toxines in the form of oxalates. A chloroform extract of the residue, a red-brown amorphous mass, constitutes "diconquinine" (Hesse, Ber. 1877, **10**, 2155). It is dextrorotatory, fluorescent in dilute sulphuric acid, and shows the thalleioquin reaction. Its salts are amorphous. According to Hesse diconquinine is to be considered as derived from the condensation of two molecules of conquinine (quinidine) with the elimination of one molecule of water. There seems to be little evidence for this view, and Hesse himself found that the molecular weight of diconquinine corresponded to the single (C_{20}) formula.

Hydrocinchonidine (cinchamidine, dihydrocinchonidine), $C_{19}H_{24}ON_2$, was first isolated by Forst and Böhringer (Ber. 1881, **14**, 1270) by oxidising commercial cinchonidine, which contains hydrocinchonidine, from *Cinchona Ledgeriana*, with cold potassium permanganate in acid solution. The cinchonidine being converted to the amphoteric substance cinchotenidine (*see under* Cinchonidine), and the hydrocinchonidine remaining for the most part unchanged, it could be readily isolated. Hydrocinchonidine is best prepared by the catalytic hydrogenation of cinchonidine, with which it is identical except that it contains an ethyl side-chain in place of the vinyl group of the latter. It is identical with Hesse's cinchamidine (Ber. 1881, **14**, 1683,) which he isolated from the mother-liquors of cinchonidine sulphate.

Hydrocinchonidine crystallises from hot dilute alcohol in hexagonal leaflets, m.p. 229°–230°, $[\alpha]_D^{15}$ −98·4° (c=2 in 97% alcohol); −144·6° (c=0·735, *i.e.* an $M/40$ solution in $0{\cdot}1N\text{-}H_2SO_4$) (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 438). It is almost insoluble in water, very sparingly soluble in ether and chloroform, and more sparingly soluble in alcohol than is cinchonidine. It is non-fluorescent and does not show the thalleioquin reaction.

The *hydrochloride*, $B\cdot HCl,2H_2O$ (Hesse, Annalen, 1882, **214**, 1) has $[\alpha]_D$ −80·4° (c=1·19 of hydrated salt in water). It is very soluble in water or alcohol. According to Heidelberger and Jacobs (J. Amer. Chem. Soc. 1919, **41**, 821) the salt crystallises from a mixture of alcohol, ether and light petroleum in anhydrous, microscopic needles and plates, m.p. 202°–203°, $[\alpha]_D^{26°}$ −89·4° (c=1·197 in water), and is readily soluble in chloroform, and fairly soluble in acetone.

The *sulphate*, $B_2\cdot H_2SO_4,7H_2O$, needles, is soluble in 57 parts of cold water.

Hydrocinchonidine is stable, it is not readily oxidised by potassium permanganate, nor isomerised by the action of hot mineral acids, but on melting the acid sulphate, hydrocinchotoxine (*see under* hydrocinchonine) is formed and on heating with hydrochloric acid in sealed tubes *epi*hydrocinchonidine is formed. On oxidation with chromic acid it gives rise to cinchoninic acid.

epi*Hydrocinchonidine*, $C_{19}H_{24}ON_2$, is epimeric with hydrocinchonidine about the carbinol ($CH\cdot OH$) group, and is obtained either by the catalytic hydrogenation of *epi*cinchonidine, or by the catalytic reduction of hydrocinchoninone or by inversion of hydrocinchonine (*q.v.*) with amyl alcoholic potassium hydroxide (Rabe, and others, Annalen, 1932, **492**, 254, 255, 263). It crystallises from ether in colourless needles, m.p. 106°, $[\alpha]_D^{20}$ +48·3° (c=1·004 in 99% alcohol). It is very readily soluble in ether and in acetone, and more so than *epi*hydrocinchonine. *epi*Hydrocinchonidine was first described, but not named, by Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H., in G.P. 330813, 1920.

Hydrocinchonidine Chloride,

$$C_9H_6N—CHCl—C_7H_{11}N—C_2H_5,$$

was prepared by Cohen and King (Proc. Roy. Soc. 1938, B, **125**, 54). The hydrochloride crystallises from alcohol, m.p. 233°–235° (*decomp.*), $[\alpha]_D^{20°}$ +24° (c=0·5 in water).

Desoxyhydrocinchonidine,

$$C_9H_6N—CH_2—C_7H_{11}N—C_2H_5,$$

has been made by the catalytic hydrogenation of cinchonidine chloride (Cohen and King, Proc. Roy. Soc. 1938, B, **125**, 56). It has also been obtained from *epi*hydrocinchonidine chloride by reduction with iron and sulphuric acid (Rabe and others, Annalen, 1932, **492**, 256), and from the hydrazone of hydrocinchoninone by heating at 180° with potassium hydroxide (*ibid.* 263, 264, 265). In the last preparation a mixture of desoxyhydrocinchonidine and desoxyhydrocinchonine (*see under* Hydrocinchonine) is formed, the desoxyhydrocinchonidine being isolated as the dianisoyltartrate from acetone. The base has m.p. 52° (*ibid.* 256) or 42°–44° (*ibid.* 265), and $[\alpha]_D$ −21·2° (c=0·4 or 0·8 in alcohol). The hydrochloride, from a mixture of methyl alcohol and ether, has m.p. 186°–188°, and $[\alpha]_D^{21°}$ +9·0° (c=1·08 in water).

Hydrocinchonine (cinchotine, dihydrocinchonine), $C_{19}H_{24}ON_2$, was first isolated from *Remijia Purdieana* by Caventou and Willm (Annalen, 1870, Suppl. **7**, 247). It occurs in most cinchona barks, and is a common component of commercial cinchonine, whence Hesse obtained it by oxidation with potassium permanganate in sulphuric acid solution at 0° (Annalen, 1873, **166**, 256). He therefore regarded it as an oxidation product of cinchonine, but Skraup showed later that it pre-exists in the "cinchonine," and that the effect of the reaction with permanganate is to oxidise the latter alkaloid, not to hydrocinchonine but to the amphoteric substance cinchotenine, and thus to facilitate the isolation of the hydrocinchonine which is left largely unattacked (Annalen, 1879, **197**, 362). Other methods for isolating hydrocinchonine depend on the crystallisation of the hydriodides (Hesse, Annalen, 1890, **260**, 213, 220; 1898, **300**, 45; Pum, Monatsh. 1895, **16**, 70), on heating with dilute sulphuric acid (the cinchonine becomes greatly altered, whereas the hydrocinchonine, remaining unchanged, can be readily separated from the resulting mixture) (Jungfleisch and Léger, Bull. Soc. chim. 1888, **49**, 747; 1901, **25**, 881), on fractional crystallisation of the dihydrobromides (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 437), and best, on the formation of a compound between cinchonine, but not hydrocinchonine, and mercuric acetate (Thron and Dirscherl, Annalen, 1935, **515**, 252). Hydrocinchonine is most conveniently prepared, however, by the catalytic hydrogenation of cinchonine, from which it differs only in containing an ethyl side-chain in place of the vinyl group of the latter.

Hydrocinchonine crystallises from alcohol in prisms and scales. Its melting-point is variously given between 267° (Buttle, Henry and Trevan, *l.c.*) and 278° (Jungfleisch and Léger, *l.c.*). Hesse found 268°–269°, and Skraup 277·3°; $[\alpha]_D$ in alcohol, between $+189{\cdot}8°$ (Rabe and others, Annalen, 1910, **373**, 100) and $+204{\cdot}5°$ (Hesse, *ibid.* 1898, **300**, 46); $[\alpha]_D$ in aqueous acid solution between $+225{\cdot}8°$ (Buttle, *et al.*) and $+227{\cdot}7°$ (Jungfleisch and Léger). Hydrocinchonine dissolves in 1,360 parts of cold water, but is more soluble in boiling water. It dissolves in 534 parts of ether, or 220 parts of alcohol at 20°, and is much less soluble than cinchonine in an alcohol-chloroform mixture.

Hydrocinchonine is stable towards mineral acids, and is unable to react additively with hydriodic acid, but heated in a sealed tube with 25% hydrochloric acid, it gives rise to some *epi*hydrocinchonine (*see below*); it can be sulphonated by means of concentrated sulphuric acid. Boiling with dilute acetic acid affords hydrocinchotoxine (*see below*). It is not readily attacked by potassium permanganate, but with chromic acid it is oxidised to hydrocinchoninone (*see below*), cinchoninic acid, cincholoipon (*see below*), cincholoiponic and loiponic acids (*see under* Cinchonine).

Hydrocinchonine Hydrochloride, $B{\cdot}HCl,2H_2O$ (Forst and Böhringer, Ber. 1881, **14**, 437; von Arlt, Monatsh. 1899, **20**, 431; Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 826) crystallises from water in needles, m.p. 216° (von Arlt), or 221°–223° (*dry*) (Heidelberger and Jacobs), $[\alpha]_D^{25}$ $+159{\cdot}3°$ (c=0·741 in water). It is soluble in 47 parts of cold water.

The *sulphate*, $B_2{\cdot}H_2SO_4$, crystallises in prisms, leaflets, or needles with 2, 6, 9, but ordinarily with 11 or $12H_2O$, depending on the conditions. The dihydrate has $[\alpha]_D^{15}$ $+164{\cdot}4°$ (c=2·5 in alcohol). The anhydrous salt, which absorbs $2H_2O$ on exposure, has m.p. 195°, is soluble in about 30 parts of cold water and in about 10 of boiling water. The dodecahydrate is efflorescent. Many other salts of hydrocinchonine are known such as the neutral and acid hydrobromide and hydriodide, acid hydrochloride and sulphate, two tartrates, and a thiocyanate.

Hydrocinchotoxine (dihydrocinchotoxine, hydrocinchonicine, cinchotinetoxine, cinchoticine),

$$C_9H_6N{-}CO{-}CH_2{-}CH_2{-}C_5H_9N{-}C_2H_5,$$

is obtained by boiling hydrocinchonine with dilute acetic acid (Kaufmann and Huber, Ber. 1913, **46**, 2919; Kaufmann, Rothlin, and Brunnschweiler, *ibid.* 1916, **49**, 2303). It has also been obtained by "partial synthesis" (Rabe and Kindler, *ibid.* 1918, **51**, 1360) from cinchoninic ester and benzoyl*homo*cincholoipon ethyl ester; (for the subsequent synthesis of *homo*cincholoipon, *see* Rabe and others, *ibid.* 1931, **64**, 2493). It is a viscous oil, $[\alpha]_D^{23}$ $+8{\cdot}8°$ (c=6·17 in alcohol). Its **N**-benzoyl-derivative has m.p. 124°, and the dipicrate of its phenylhydrazone melts at 215°. The free toxine, which is readily soluble in ether or in dilute alcohol, can be brominated, and is then on treatment with alkali converted into hydrocinchoninone (*see below*). Hydrocinchotoxine gives purple colorations with nitrobenzene containing nitrothiophene and with diazobenzenesulphonic acid.

epi*Hydrocinchonine*, $C_{19}H_{24}ON_2$, is epimeric with hydrocinchonine about the carbinol ($CH{\cdot}OH$) group. It was first obtained but not named by Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H., G.P. 330813/1920, by the reduction of hydrocinchoninone with aluminium or zinc in alcoholic solution in presence of sodium ethoxide. It can also be obtained from hydrocinchoninone by catalytic reduction, from hydrocinchonine by epimerisation with amyl alcoholic potash, and from *epi*cinchonine by catalytic hydrogenation (Rabe and others, Annalen, 1932, **492**, 252–255, 263). In all cases except the last, a mixture of hydrocinchonine, hydrocinchonidine, *epi*hydrocinchonine, and *epi*hydrocinchonidine is produced. The first two naturally occurring alkaloids are readily removed by taking advantage of their sparing solubility in ether. The two residual *epi*-bases are separated mechanically and by fractional crystallisation from ether and from acetone. *epi*Hydrocinchonine crystallises from acetone in colourless, tapering prisms, m.p. 126°, $[\alpha]_D^{19}$ $+88{\cdot}4°$ (c=1·0012 in 99% alcohol). It is readily soluble in ether or acetone, and very readily so in alcohol or benzene.

Hydrocinchoninone,

$$C_9H_6N{-}CO{-}C_7H_{11}N{-}C_2H_5,$$

is obtained in low yield by the gentle oxidation of hydrocinchonine with chromic acid (Rabe, Naumann and Kuliga, Annalen, 1909, **364**, 349), but is best prepared indirectly from hydrocinchotoxine by way of the **C**-bromo derivative (Kaufmann and Huber, Ber. 1913, **46**, 2920; Kaufmann and Haensler, *ibid.* 1917, **50**, 703; Rabe and Kindler, *ibid.* 1918, **51**, 1365). It separates in pale yellow crystals from 60% alcohol, has m.p. 138° (Rabe) or 130°

(Kaufmann) and $[\alpha]_D$ (final value) on the average +76° in alcohol (c=from 2 to 4). The hydrochloride, which is quite white, crystallises from alcohol and ether and has m.p. 265°. The oxime is amorphous. For the mutarotation of hydrocinchoninone, *see* Rabe and others (Annalen, 1910, **373**, 118).

Hydrocinchonine Chloride,

$$C_9H_6N—CHCl—C_7H_{11}N—C_2H_5,$$

is made by treating dry hydrocinchonine hydrochloride in chloroform with phosphorus pentachloride (Koenigs and Hoerlin, Ber. 1894, **27**, 2291 ; Jacobs and Heidelberger, J. Amer. Chem. Soc. 1922, **44**, 1087). Crystallised from etherit has m.p. 85°–87° (*indef.*) or with $1{\cdot}5H_2O$ from aqueous acetone, m.p. 70° (*indef.*). The latter form, on drying in a desiccator, becomes amorphous and has $[\alpha]_D^{24}$ +36·4° (c=1·001 in alcohol). It is very readily soluble in organic solvents. The *hydrochloride*, m.p. 227°–228°, $[\alpha]_D^{23}$ +48·8° (c=1·107 in water), crystallises from 85% alcohol, and is sparingly soluble in cold water or alcohol, but more readily so in the boiling solvent. The hydrobromide is very sparingly soluble in water.

Desoxyhydrocinchonine,

$$C_9H_6N—CH_2—C_7H_{11}N—C_2H_5,$$

is made either by reducing hydrocinchonine chloride with iron in dilute sulphuric acid (E. G. W. Schmidt, Dissertation, Jena, 1913; Jacobs and Heidelberger, J. Amer. Chem. Soc. 1922, **44**, 1088), or by hydrogenating desoxycinchonine or cinchene using a palladium-calcium carbonate catalyst (Schöpf and Schmidt, Annalen, 1928, **465**, 127), or by heating the hydrazone of hydrocinchoninone with powdered potassium hydroxide (Rabe and von Riegen, Annalen, 1932, **492**, 263). Desoxyhydrocinchonine base crystallises from moist ether or from aqueous acetone with $2H_2O$, m.p. 60°, $[\alpha]_D^{30}$ +113·8° (c=1·014 in alcohol). The water is lost in dry air or in a desiccator, and the base becomes amorphous. It separates in the anhydrous condition from light petroleum or from absolute ether, and then has m.p. 74°, $[\alpha]_D^{20}$ +147° in alcohol. It is easily soluble in organic solvents. The hydrochloride crystallises from alcohol in narrow glistening plates and prisms, m.p. 197°–199°, $[\alpha]_D^{24}$ +69·3° (c=1·068 in water). The salt is fairly soluble in alcohol, very readily so in methyl alcohol or in chloroform, but less so in acetone. The *hydriodide* has m.p. 230°–231°.

Hydrocinchene,

$$C_9H_6N—CH{=}C < C_6H_{10}N—C_2H_5,$$

is prepared by boiling hydrocinchonine chloride with alcoholic potash (Koenigs and Hoerlin, Ber. 1894, **27**, 2291 ; Koenigs, *ibid.* 1895, **28**, 3146 ; J. pr. Chem. 1900, [ii], **61**, 44 ; *see also* Koenigs, Ber. 1894, **27**, 1504). It crystallises from aqueous methyl alcohol in leaflets, m.p. 145°. With 25 % phosphoric acid at 170° it is hydrolysed to lepidine (*q.v. under* Cinchonine) and cincholoipon (*see below*), but does not react with hydrobromic acid (distinction from cinchene). It is isomeric with, but distinct from, desoxycinchonine.

Oximinoethylquinuclidine, ethylquinuclidoneoxime, $HO—N{=}C < C_6H_{10}N—C_2H_5$, is formed together with cinchoninic acid from hydrocinchoninone, when this ketone, dissolved in cold alcoholic sodium ethoxide, is treated with a little more than one molecular proportion of amyl nitrite (Rabe and Naumann, Annalen, 1909, **365**, 363). It crystallises in white needles from a mixture of light petroleum (b.p. 60°–65°) and ethyl acetate, and has m.p. 133°–134°. It is readily soluble in water, alcohol, ether, or ethyl acetate, but less so in light petroleum. On hydrolysis with hydrochloric acid, the bicyclic system undergoes rupture, and there are formed hydroxylamine and cincholoipon.

Cincholoipon, 3-ethylpiperidine-4-acetic acid, $C_2H_5—C_5H_9N—CH_2—CO_2H$, was first discovered by Skraup (Monatsh. 1888, **9**, 805) in the products of oxidation of cinchonine and quinine with chromic acid. It was shown by Koenigs, however (Ber. 1894, **27**, 1504 ; with Hoerlin, *ibid.* 2290), that the cincholoipon was derived not from these alkaloids but from the hydro-alkaloids present in the commercial materials. Cincholoipon can be prepared either by the hydrolysis of hydrocinchene with 25% phosphoric acid at 170°, or by oxidation of hydrocinchonine with chromic acid (Koenigs, and Koenigs and Hoerlin, *l.c.*). It has also been prepared by the reduction of meroquinene (*q.v. under* Cinchonine) either with zinc and hydriodic acid (Koenigs, *ibid.* 1902, **35**, 1350), or better catalytically (Kaufmann, Zeller and Huber, *ibid.* 1913, **46**, 1830). It can also be prepared from hydrocinchoninone, by the action of amyl nitrite followed by hydrolysis (*see* Oximinoethylquinuclidine, *above*). Its **N**-methyl derivative is readily obtained by subjecting *iso*nitroso-**N**-methylcinchotoxine to the Beckmann transformation ; the easily isolable **N**-methyl derivative of the nitrile of cincholoipon is then formed (Rabe and Ackermann, Ber. 1907, **40**, 2013). Cincholoipon crystallises from methyl alcohol and has m.p. 236°. It is soluble in water. The *hydrochloride* consists of yellow rhombic crystals, m.p. 200°, readily soluble in water or in alcohol, but not in ether. The salt has $[\alpha]_D^{23}$ −5·6° (c=10 in water). *Cincholoipon ethyl ester hydrochloride* has m.p. 158° and $[\alpha]_D^{22}$ +5·71° (c=8·29 in water).

Hydroquinidine, $C_{20}H_{26}O_2N_2$, occurs in commercial quinidine, sometimes in large amount. It was first isolated from this source by Forst and Böhringer by oxidation with potassium permanganate in acid solution at 0° (Ber. 1881, **14**, 1954; 1882, **15**, 520, 1656), the effect being to oxidise the unsaturated quinidine to the alkali-soluble quitenidine, and thus to facilitate the isolation of the hydroquinidine. It is best prepared by catalytic hydrogenation of quinidine, from which it differs only in having an ethyl side-chain in place of a vinyl group. It has been synthesised by Rabe, Huntenburg, Schultze and Volger (Ber. 1931, **64**, 2487).

Hydroquinidine crystallises from ether (stout plates) or alcohol (needles), and is said to contain $2{\cdot}5H_2O$ which is easily expelled, but the existence of such a hydrate is doubtful (Giemsa and Halberkann, Ber.1921, **54**, [B], 1201). The dry base melts at 169° and has $[\alpha]_D^{20}$ +231·3° (*c*=2·0216 in alcohol), and +299° (*c*=0·815, *i.e.* an *M*/40 solution in 0·1 *N*-H_2SO_4). It is sparingly soluble in ether, but dissolves readily in hot alcohol. It gives the thalleioquin reaction, and fluoresces in dilute sulphuric acid solution. Under the influence of hot mineral acids it is demethylated to hydrocupreidine (*v. infra*), but does not undergo isomerisation. It is fairly stable towards potassium permanganate, but with chromic acid is oxidised to quininic acid (*q.v. under* Quinine), and cincholoipon (*v. supra*).

Hydroquinidine Hydrochloride, $B \cdot HCl$, is readily soluble in water, melts at 273°–274°, and has $[\alpha]_D^{26}$ +183·9° (*c*=1·3 in water) (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 826).

Hydroquinidine Sulphate, $B_2 \cdot H_2SO_4$, separates from water above 20° in needles containing $3H_2O$ (Giemsa and Halberkann) or $2H_2O$ (Hesse). The anhydrous salt, m.p. 214°, does not absorb water on re-exposure. When crystallised below 10°, the sulphate separates in prisms, and these are so efflorescent that it is difficult to determine their initial water content, which is given as 8 and $12H_2O$, but may be as high as 18 H_2O. The hydrate stable in the air appears to be $B_2 \cdot H_2SO_4,2H_2O$, for the anhydrous salt reabsorbs that amount on exposure. Hydroquinidine sulphate dissolves in 92·3 parts of water at 16°.

The *dihydrochloride* has been used to separate quinidine and hydroquinidine (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 434); the *dihydrobromide* has been described by Emde (Helv. Chim. Acta, 1932, **15**, 575). The *neutral tartrate*, $B_2 \cdot C_4H_6O_6,2H_2O$, is readily soluble in water, but the *acid tartrate*, $B \cdot C_4H_6O_6,3H_2O$, is sparingly soluble.

epi*Hydroquinidine*, $C_{20}H_{26}O_2N_2$, is epimeric with hydroquinidine about the carbinol ($CH \cdot OH$) group. It is obtained either by heating hydroquinine with amyl alcoholic potassium hydroxide, or by the catalytic reduction of hydroquininone, or by catalytic hydrogenation of *epi*quinidine. In each case except the last, a mixture of hydroquinine, hydroquinidine, *epi*hydroquinine and *epi*hydroquinidine is produced. After removing the first two naturally occurring alkaloids as neutral and acid tartrate respectively, the two *epi*-bases are separated as neutral dibenzoyltartrates from benzene. The *epi*hydroquinidine so obtained from the more soluble component is finally purified by recrystallisation of the base from ether. *epi*Hydroquinidine has been synthesised (Rabe and others, Ber. 1931, **64**, 2499). It forms colourless, flat prisms from ether, m.p. 122°, $[\alpha]_D^{16}$ +73·7° (*c*=0·3324 in alcohol), is very readily soluble in alcohol, fairly soluble in ether, and is strongly fluorescent in sulphuric acid solution. Its dibenzoyltartrate, m.p. 156°–157°, is sparingly soluble in water, ether, benzene, or cold alcohol, but readily so in hot alcohol (Rabe and others, Annalen, 1932, **492**, 253, 256, 257, 261).

Hydroquinidine Chloride,

$CH_3O \cdot C_9H_5N—CHCl—C_7H_{11}N—C_2H_5$,

is prepared from dry hydroquinidine hydrochloride and phosphorus pentachloride in chloroform solution (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1497). It crystallises from light petroleum in cream-tinted plates, m.p. 93·5°–95°, $[\alpha]_D^{22}$ +20° (*c*=0·6 in alcohol). The *hydrochloride*, needles from alcohol, m.p 208°–209°, $[\alpha]_D^{25}$ +39·7° (*c*=0·795 in water), is readily soluble in water and in methyl alcohol, less so in ethyl alcohol or in chloroform, and sparingly so in acetone.

Desoxyhydroquinidine,

$CH_3O—C_9H_5N—CH_2—C_7H_{11}N—C_2H_5$,

is obtained by reducing hydroquinidine chloride with iron filings in dilute sulphuric acid (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1497). It has also been made similarly from *epi*hydroquinidine chloride (Rabe and others, Annalen, 1932, **492**, 258), and the following particulars are taken from these two sources (*cf.* Giemsa and Halberkann, Ber. 1921, **54**, 1203). Desoxyhydroquinidine crystallises from 60% alcohol with $2H_2O$, m.p. 85°–87°, $[\alpha]_D^{22 \cdot 5}$ +167·3° (*c*=1·124 in alcohol). The anhydrous base melts lower at 68·5°–70°.

It is readily soluble in alcohol, acetone, chloroform, or benzene and less so in ether. It gives the thalleioquin reaction and fluoresces in dilute sulphuric acid solution (purple). Its hydrobromide melts at 151°–152°.

Hydrocupreidine, $C_{19}H_{24}O_2N_2$, was first obtained by Heidelberger and Jacobs (J. Amer. Chem. Soc. 1919, **41**, 827) by the demethylation of hydroquinidine with 4 parts of boiling 40% hydrobromic acid at 125°. It can also be prepared from hydroquinidine with strong sulphuric acid, the resulting hydrocupreidine sulphonic acid being saponified by heating with dilute hydrochloric or sulphuric acid (Giemsa and Bonath, Ber. 1925, **58**, [B], 93), or directly by boiling with 60% sulphuric acid (Henry and Solomon, J.C.S. 1934, 1929) Hydrocupreidine crystallises from aqueous alcohol (Heidelberger and Jacobs) or from acetone (Henry and Solomon) as an indefinite hydrate which is difficult to dry without discoloration ; the hydrate melts at 170°. The anhydrous base melts indefinitely at 195°. According to Giemsa and Bonath the base crystallises from absolute alcohol, and then has m.p. 193°. The specific rotations given for the dry base in alcohol are widely different: +253·4° (Heidelberger and Jacobs), +242·5° (Giemsa and Bonath), +227·2° (Henry and Solomon). The base is readily soluble in cold alcohol, less readily in chloroform or acetone, and sparingly in ether. It is non-fluorescent, and does not give a coloration with bromine water and ammonia. The *hydrochloride* crystallises from 50% alcohol in rosettes of needles which are not anhydrous, as stated by Henry and Solomon (*l.c.*), but contain $1H_2O$; the anhydrous salt melts at 232°, and has $[\alpha]_D$ +194° in water. The *dihydrchloride* is sparingly soluble in dilute hydrochloric acid. For other salts and for the ethyl ether of hydrocupreidine, *see* Heidelberger and Jacobs (*l.c.*), and for other homologous alkyl ethers, *see* Ghosh and Chatterjee (J. Indian Chem. Soc. 1931, **8**, 257 ; 1932, **9**, 83 ; Buttle, Henry, Solomon, Trevan and Gibbs, Biochem. J. 1938, **32**, 52).

Hydroquinine, $C_{20}H_{26}O_2N_2$, accompanies quinine in cinchona barks and in commercial quinine sulphate. It was first isolated by Hesse (Ber. 1882, **15**, 856 ; Annalen, 1887, **241**, 257, 286) from quinine sulphate mother-liquors, by taking advantage of the fact that hydroquinine acid sulphate, $B{\cdot}H_2SO_4$, or hydroquinine dihydrobromide, $B{\cdot}2HBr$, is more soluble in water than the corresponding quinine salt. Quinine can in this way be completely freed from hydroquinine, but the latter can only be prepared in the pure state by oxidising with potassium permanganate the mixture of quinine and hydroquinine obtained in the mother liquors ; the quinine becomes oxidised to the alkali-soluble quitenine, and the hydroquinine, being left largely unattacked, can then be readily isolated. It is, however, best prepared by the catalytic hydrogenation of quinine, from which it differs only in that it has an ethyl side-chain in place of the vinyl group of the latter. This process has in the last decade or two acquired much technical importance, partly because of the demand for hydroquinine itself as a therapeutic agent, and partly because it constitutes the starting material for the manufacture of the hydrocupreine ethers (" optochin," " vuzin "). Early examples of such catalytic processes can be found in the following patents : G.P. 234137/1911, 252136/1912, 267306/1913; B.P. 3948/1912. For details of processes, *see* CATALYSIS IN INDUSTRIAL CHEMISTRY, Vol. II, p. 422.

Hydroquinine base is precipitated by sodium hydroxide solution from aqueous solutions of its salts, when it separates in amorphous flakes which gradually become crystalline and contain $2H_2O$. This form turns to a soft rubbery mass below 100°, but the anhydrous form, which crystallises from ether or benzene, melts at 172·3° (Lenz, Z. anal. Chem. 1888, **27**, 561) and has $[\alpha]_D^{20}$ $-142{\cdot}2°$ ($c=2{\cdot}4$ in 95% alcohol) (Hesse), or $-235{\cdot}7°$ ($c=0{\cdot}815$, *i.e.* an $M/40$ solution in $0{\cdot}1N$-H_2SO_4) (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 436). It is readily soluble in most organic solvents, including ether, but not in water or alkalis ; it nevertheless dissolves appreciably in ammonia solution. Hydroquinine is fluorescent in dilute sulphuric acid solution, and gives the thalleioquin reaction. It is relatively stable towards permanganate, but is oxidised by chromic acid to quininic acid (*q.v. under* Quinine) and cincholoipon (*q.v. under* Hydrocinchonine). On melting its acid sulphate, or on boiling with dilute acetic acid, it is transformed to hydroquinotoxine (*v. infra*). With strong mineral acids (HCl, HBr, HI, H_2SO_4) or aluminium chloride it undergoes demethylation (*see* " Hydrocupreine " *below*), but not isomerisation. Hydroquinine is bitter to the taste, and is equal or superior in antimalarial activity to quinine.

Hydroquinine Hydrochloride, $B{\cdot}HCl,2H_2O$, crystallises from water in prisms. The anhydrous salt melts at 206°–208°, and has $[\alpha]_D^{21}$ $-123{\cdot}9°$ ($c=1{\cdot}113$ in water). It also crystallises from a mixture of acetone and ether with $0{\cdot}5H_2O$. It is readily soluble in water, alcohol or acetone, but not in ether (Hesse, Annalen, 1887, **241**, 264 ; Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 820).

Hydroquinine Sulphate, $B_2{\cdot}H_2SO_4$, crystallises from water in needles containing $6H_2O$ when stable, but probably with $8H_2O$ at first. The salt is soluble in 348 parts of cold water, and when anhydrous re-absorbs 4 or $6H_2O$ on exposure. The *acid sulphate*, $B{\cdot}H_2SO_4$, crystallises with $3H_2O$ and is extremely soluble in water. The *dihydrobromide* crystallises with $3H_2O$, and the anhydrous salt has $[\alpha]_D^{15}$ $-152{\cdot}5°$ in water. Many other salts of hydroquinine are known. It forms loose compounds with several other cinchona alkaloids and also with anethole ; it forms an amorphous acetyl- derivative, a crystalline benzoyl- derivative (m.p. 102°–107°), and a methiodide.

Hydroquinotoxine (hydroquinicine),

$$CH_3O{-}C_9H_5N{-}CO{-}CH_2{-}CH_2{-}C_5H_9N{-}C_2H_5,$$

is prepared from hydroquinine either by heating the acid sulphate at 140° (Hesse, Annalen, 1887, **241**, 273) or by boiling in dilute acetic acid (Rabe, Ber. 1912, **45**, 2927; Kaufmann and Huber, *ibid.* 1913, **46**, 2921 ; Heidelberger and Jacobs, J. Amer. Chem. Soc. 1922, **44**, 1092). It has been synthesised by Rabe and his co-workers (Ber. 1931, **64**, 2497 ; *see also* Rabe and Kindler, *ibid.* 1919, **52**, 1842). It is a yellow varnish, $[\alpha]_D^{15}$ $-17°$ ($c=3$ in water with $3HCl$), easily soluble in alcohol, ether, or chloroform. Its solution in dilute sulphuric acid is yellow, but non-fluorescent, and it gives the thalleioquin reaction. The *sulphate*, $B_2{\cdot}H_2SO_4$, crystallises from a mixture of aqueous alcohol and acetone with $3H_2O$; the anhydrous salt has m.p. 174°–176°, $[\alpha]_D^{21{\cdot}5}$ $-8{\cdot}3°$ ($c=0{\cdot}968$ in water). Oxalic acid precipitates an amorphous *oxalate*, which is soluble in chloroform (distinction from quinotoxine); the *dibenzoyltartrate* melts at 170°.

epi*Hydroquinine*, $C_{20}H_{26}O_2N_2$, is epimeric with hydroquinine about the carbinol ($CH{\cdot}OH$) group. It can be prepared either from hydroquinine by epimerisation with amyl alcoholic potassium hydroxide, or from hydroquinone by catalytic reduction, or by the catalytic hydrogenation of *epi*quinine. In the first two cases there is formed a mixture of hydroquinine, hydroquinidine, *epi*hydroquinine and *epi*hydroquinidine. The first two naturally occurring alkaloids are removed as neutral and acid tartrate respectively ; the two *epi*-bases are then separated as neutral dibenzoyltartrates from benzene. The *epi*hydroquinine so obtained from the more sparingly soluble component is finally purified by recrystallisation of its hydrochloride from acetone. Attempts to crystallise the base have so far failed ; it is a viscous oil, $[\alpha]_D^{22}$ $+32°$ ($c=0{\cdot}95$ in alcohol), readily soluble in organic solvents, and showing a strong blue fluorescence in sulphuric acid solution. The dibenzoyltartrate, m.p. 151° crystallises from acetone, and is sparingly soluble in water, benzene, light petroleum or ether readily so in alcohol or chloroform (Rabe and co-workers, Annalen, 1932, **492**, 253, 256, 257, 260).

Hydroquininone,

$$\mathrm{CH_3O{-}C_9H_5N{-}CO{-}C_7H_{11}{-}C_2H_5},$$

was first prepared by Irschick (Dissertation, Jena, 1913) by the gentle oxidation of hydroquinine with chromic acid. It is best prepared indirectly from hydroquinotoxine. By brominating in hydrobromic acid solution the C-bromotoxine is obtained, which, on treatment with sodium ethoxide in alcoholic solution, gives rise to the desired ketone (Kaufmann and Huber, Ber. 1913, **46**, 2922). It has been synthesised by Rabe and his co-workers (Ber. 1931, **64**, 2497; *see also* Rabe and Kindler, *ibid.* 1919, **52**, 1845). Hydroquininone crystallises from ether in yellowish needles or leaflets, m.p. 99°; it shows mutarotation: $[\alpha]_D$ (final value) $+73\cdot15°$ ($c=1\cdot784$ in alcohol) (Kaufmann and Huber; Rabe and Kindler; Irschick's ketone, prepared by direct oxidation, and Rabe's synthetic ketone have lower rotations, $+65\cdot0°$ and $+68\cdot8°$ respectively). The picrate melts at 224°.

Hydroquinine Chloride,

$$\mathrm{CH_3O{-}C_9H_5N{-}CHCl{-}C_7H_{11}N{-}C_2H_5},$$

is prepared by the action of phosphorus pentachloride on dry hydroquinine dihydrochloride dissolved in cold chloroform (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1491; Giemsa and Halberkann, Ber. 1921, **54**, [B], 1194). It crystallises from dilute alcohol or from petroleum spirit (b.p. 80°–90°) in cream-coloured rhombs, m.p. 144°, $[\alpha]_D^{21\cdot5}$ $+42\cdot1°$ ($c=1\cdot365$ in alcohol) or $+43°$ ($c=3\cdot0136$ in alcohol). Hydroquinine chloride is readily soluble in alcohol, acetone, chloroform, or benzene, less readily in ether, fairly soluble in boiling but very sparingly soluble in cold petroleum spirit. It is a light-sensitive substance which gives the thalleioquin reaction. Aqueous acid solutions are yellow, but non-fluorescent. The *hydrochloride*, **B·HCl**, m.p. 232°–233°, $[\alpha]_D^{20\cdot5}$ $-2\cdot9°$ ($c=1\cdot197$ in water) crystallises from 50% alcohol, and is somewhat sparingly soluble in water or alcohol.

Desoxyhydroquinine,

$$\mathrm{CH_3O{-}C_9H_5N{-}CH_2{-}C_7H_{11}N{-}C_2H_5},$$

is obtained by reducing hydroquinine chloride with iron in dilute sulphuric acid solution (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1492; Giemsa and Halberkann, Ber. 1921, **54**, 1198), or in the same manner from *epi*-hydroquinine chloride (Rabe and others, Annalen, 1932, **492**, 258). Desoxyhydroquinine crystallises from aqueous acetone in colourless, silky needles which contain $3H_2O$ and melt at 69°, solidify on further heating, and melt again at 95°. The $3H_2O$ is readily lost in a desiccator; the anhydrous base is oily, absorbs $2H_2O$ from the air, and in doing so crystallises. The trihydrate has $[\alpha]_D^{24}$ $-77\cdot5°$ ($c=1\cdot244$ in alcohol) and is readily soluble in organic solvents; it gives the thalleioquin and fluorescence tests. The *hydrochloride*, **B·HCl**, crystallises from acetone in anhydrous needles, m.p. 179°–180°, $[\alpha]_D^{22\cdot5}$ $-6\cdot8°$ ($c=1\cdot034$ in water). The salt dissolves readily in water, alcohol, methyl alcohol, chloroform, or hot acetone or benzene, but sparingly in cold acetone or benzene.

Hydroquinene,

$$\mathrm{CH_3O{-}C_9H_5N{-}CH{=}C{<}C_6H_{10}N{-}C_2H_5},$$

is prepared by boiling hydroquinine chloride with alcoholic potassium hydroxide (Giemsa and Halberkann, Ber. 1921, **54**, [B], 1194). It crystallises from a mixture of ether and light petroleum in colourless rosettes of coffin-shaped needles, and on recrystallisation from dilute alcohol or acetone, separates with $2H_2O$. The anhydrous substance melts at 78°–79°, and has $[\alpha]_D^{20}$ $+29\cdot5°$ ($c=2\cdot678$ in alcohol). It is readily soluble in the usual organic solvents, except in light petroleum. Hydroquinene gives the thalleioquin test, fluoresces in dilute nitric acid solution, and is instantly attacked by potassium permanganate. The *hydrochloride* melts at 209°.

Hydrocupreine, $C_{19}H_{24}O_2N_2$, is prepared by demethylating hydroquinine with hot hydrochloric (Hesse, Annalen, 1887, **241**, 280), hydrobromic (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 821), or hydriodic acid (Pum, Monatsh. 1895, **16**, 73), with aluminium chloride in nitrobenzene solution (Oberlin, Arch. Pharm. 1927, **265**, 270), or with concentrated sulphuric acid, when a sulphonic acid is formed which is hydrolysed by boiling with dilute hydrochloric or sulphuric acid (Giemsa and Bonath, Ber. 1925, **58**, [B], 89, 92). It can also be obtained by the catalytic hydrogenation of cupreine (Giemsa and Halberkann, *ibid.* 1918, **51**, 1328), but best, perhaps, by boiling hydroquinine with 60% sulphuric acid. Apart from demethylation, no change takes place, for hydroquinine is regenerated when hydrocupreine is methylated by means of diazomethane (Oberlin.)

Hydrocupreine is precipitated by means of ammonia as a micro-crystalline powder containing $2H_2O$, but crystallises (if pure) from alcohol, dilute alcohol, or from a mixture of chloroform and benzene in the anhydrous condition. From benzene alone it separates as a jelly. It becomes amorphous on heating below its melting-point, and this accounts for a divergence among the published figures; Hesse and Pum give m.p. 170°; Giemsa and Halberkann record 204°, while Giemsa and Bonath, seven years later, record 186°; according to Heidelberger and Jacobs hydrocupreine becomes a glassy mass filled with bubbles of gas at 185°–190°, and this does not become completely liquid until 230°. The specific rotation of hydrocupreine in alcohol is given variously between the extremes $-148\cdot7°$ (Heidelberger and Jacobs) and $-159\cdot2°$ (Giemsa and Bonath). Hydrocupreine is readily soluble in alcohol or chloroform, and as a phenol dissolves freely in caustic alkalis. It is sparingly soluble in ether or ethyl acetate, almost insoluble in light petroleum or water, and dissolves with difficulty in ammonia solution. Hydrocupreine is non-fluorescent and does not give the thalleioquin reaction although Hesse claims to have obtained the green colour by using bleaching powder. Aqueous solutions of the neutral salts, like those of cupreine, are of an intensely yellow colour, which is immediately discharged on the addition of mineral acids. *Hydrocupreine hydrochloride* ($B{\cdot}HCl$) crystallises from water acidified with hydrochloric acid in anhydrous needles, *decomp.* 255°–280°, melting at the latter temperature, $[\alpha]_D^{22\cdot5}$ $-132\cdot3°$ ($c=0\cdot945$ in alcohol); it is sparingly soluble in water, acetone, or chloroform, readily dissolves in alcohol and very readily in methyl alcohol. The *dihydrochloride*, $B{\cdot}2HCl,H_2O$, melts at 224°. The *neutral sulphate*, $B_2{\cdot}H_2SO_4$, is anhydrous and very sparingly soluble in water or in alcohol. The *acid sulphate*, $B{\cdot}H_2SO_4$, separates with $4H_2O$; the anhydrous salt, m.p. 203°, reabsorbs $1H_2O$ on exposure. The *tartrate*, $B_2{\cdot}C_4H_6O_6,2H_2O$, melts at 242°. Other salts prepared include the dihydrobromide and acid nitrate.

Hydrocupreine gives rise to a toxine, hydrocupreinotoxine (hydrocupreicine), in the ordinary way, but a number of derivatives such as hydrocupreine bromide and desoxyhydrocupreine have been obtained by demethylating the corresponding hydroquinine derivatives. As a phenol, hydrocupreine, in common with cupreine, couples with diazonium solutions, giving rise to an interesting series of dyes.

A considerable amount of attention has been given to the alkyl ethers of hydrocupreine and hydrocupreinotoxine since the discovery of their striking bactericidal action by Morgenroth and collaborators, who investigated the complete series from ethyl to cetyl (C_{16}). Those interested in the results of these biological investigations and their possible therapeutic application should consult "The Therapeutic Agents of the Quinoline Group" by von Oettingen (Chemical Catalog Co. Inc., New York, 1933), "Handbuch der Chemotherapie" by Fischl and Schlossberger (Fischer's Medizinische Buchhandlung, Leipzig, 1932) and "Recent Advances in Chemotherapy" by Findlay (J. and A. Churchill, London, 1930). For the preparation of some of these substances, *see* Vereinigte Chininfabriken, Zimmer & Co. G.m.b.H., G.P. 254712, 1912, 344140/1921; Giemsa and Halberkann, Ber. 1918, **51**, 1332; Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 824; 1922, **44**, 1097; Slotta and Behnisch, Ber. 1933, **66**, [B], 360, and for the entire series up to C_{11}, *see* Buttle, Henry, Solomon, Trevan and Gibbs, Biochem. J. 1938, **32**, 51. Among the better known products are *iso*amylhydrocupreine dihydrochloride ("eucupin"), *sec*-octylhydrocupreine dihydrochloride ("vuzin") and *ethylhydrocupreine hydrochloride* ("optochin"),

$$C_2H_5O{-}C_9H_5N{-}CH(OH){-}C_7H_{11}N{-}C_2H_5{\cdot}HCl,$$

which is recognised in the "United States Pharmacopœia," XI. The salt readily crystallises from a mixture of acetone and ether, m.p. 252°–254°, $[\alpha]_D^{21}$ $-123\cdot6°$ ($c=0\cdot959$ in water). It is readily soluble in water or alcohol. The base on the market is also amorphous, but has been obtained crystalline from toluene; the anhydrous base has m.p. 123°–128° and $[\alpha]_D$ $-136\cdot2°$ ($c=1\cdot005$ in alcohol).

Javanine, of undetermined composition, was isolated by Hesse (Ber. 1877, **10**, 2162) from the bark of *Cinchona Calisaya* var. *javanica*. It crystallises from water in rhombic leaflets, is readily soluble in ether, forms a crystalline oxalate, and dissolves in dilute sulphuric acid with an intensely yellow colour.

Niquidine.—See under Quinidine.

Paricine, $C_{16}H_{18}ON_2$, was discovered by Winckler (Jahresbericht, 1845, **27**, 338) in the barks of *Buena hexandra* and *Cinchona lutea*. Later, Hesse found it in *C. succirubra* of Darjeeling (Pharm. J. 1870, **1**, 344; Annalen, 1873, **166**, 263). It is an amorphous, yellow powder, m.p. 116°, soluble in water, alcohol, ether or light petroleum. Its salts are also amorphous, and its nitrate is insoluble.

Quinamine, $C_{19}H_{24}O_2N_2$, was isolated from the bark of *Cinchona succirubra* by Hesse (Ber. 1872, **5**, 265; *see also ibid.* 1877, **10**, 2157; Annalen, 1873, **166**, 266; 1881, **207**, 288). It occurs only in small quantities, but is widely distributed, one of the richest sources being *Cinchona Ledgeriana*. Oudemans (Annalen, 1879, **197**, 49) found that the total alkaloids of *C. succirubra* contained 4·5% of quinamine. It is best isolated from quinine sulphate mother-liquors (*see* foregoing references and de Vrij, Pharm. J. 1874, **4**, 609; Howard, *ibid.* 1875, **5**, 1) by removing quinine and cinchonidine as tartrates, and cinchonine as thiocyanate. The quinamine crystallises from a solution of the residual bases in 80% alcohol, or may be purified by crystallisation of the nitrate. The base crystallises in long, anhydrous needles, m.p. 172°, $[\alpha]_D^{15}$ $+93\cdot4°$ ($c=2$ in chloroform), or $+104\cdot5°$ in alcohol. It is almost insoluble in water, sparingly so in alcohol, and fairly soluble in ether, it gives a rich yellow coloration with concentrated sulphuric acid in the presence of a little nitric acid; on diluting with water, the colour changes through purple to pink. Quinamine is a monoacidic base, and its acid salts are amorphous; the neutral salts, of which a fairly large number have been prepared, crystallise well. It contains no methoxyl group, is readily oxidised, and is very unstable towards acids, a variety of products being formed (Hesse, Annalen, 1881, **207**, 292 *et seq.*). Very mild treatment, such as boiling with 1% sulphuric acid, or even standing at the ordinary temperature in 13% hydrochloric acid, suffices to isomerise quinamine to *quinamidine* (m.p. 93°, $[\alpha]_D$ $+4\cdot5°$ in alcohol). This is best prepared (*ibid.* 299) by heating quinamine with 5 parts of 10% tartaric acid solution for 2 hours. Together with quinamidine is always formed in smaller amount another isomeride, *quinamicine* (m.p. 109°, $[\alpha]_D$ $+3\cdot8°$ in alcohol), which is obtained also from conquinamine (*q.v.*), but in greatest amount when an alcoholic solution of quinamine acid sulphate containing a little glycerol is evaporated at 60°–80°, and the residue heated at 100° for several minutes (*idem, ibid.* 303). If the residue is heated at 120°–130° instead of at 100°, an amorphous substance *proto*quinamicine, $C_{17}H_{20}O_2N_2$, is formed (*idem, ibid.* 305).

When boiled with hydrochloric acid (sp.gr. 1·125) or with 25% sulphuric acid for 3 minutes, quinamine is dehydrated to apo*quinamine* ($C_{19}H_{22}ON_2$, *idem, ibid.* 294) (m.p. 114°; base optically inactive, *hydrochloride*,

$$B{\cdot}HCl,\tfrac{1}{2}H_2O,$$

lævorotatory). *apo*Quinamine is formed in the same way also from quinamicine or conquinamine (*q.v.*). Quinamine and *apo*quinamine give rise to one and the same acetyl-derivative, which on hydrolysis furnishes the latter base. On heating at 140° with hydrochloric acid saturated at −17° quinamine is converted into a rubbery mass, which is insoluble in dilute acids, or in ordinary organic solvents.

Quinetum.—This name was used by de Vrij to describe the total alkaloids of *C. succirubra*, which in the early days of cinchona-planting he recommended as the most economical method of utilising cinchona alkaloids. The preparation was also known as "cinchona febrifuge." When *Cinchona succirubra* was supplanted by species yielding bark richer in quinine, it became difficult to supply "quinetum" and the demand was met in two different ways. The residues of the total alkaloids of "factory bark," after the removal of quinine, were made into a quinetum substitute by the return of some quinine and the product was known as "cinchona febrifuge." Its variability in composition has frequently been commented upon (*see*, for example, League of Nations, Health Section, C.H. Malaria/158, Geneva 14/4/1931; Howard, Trans. Roy. Soc. Trop. Med. Hyg. 1925, **18**, 358; Goodson and Henry, Quart. J. Pharm. 1930, **3**, 238) and it is desirable that it should be replaced by a standardised preparation such as totaquina (p. 132).

Cinchona febrifuge was sold principally to indigent natives in tropical countries. There was also a certain demand for quinetum in Europe, and under the new conditions this demand was met by mixtures of the crystalline alkaloids of cinchona, but as there was no standard this product was also variable (League of Nations, Health Section, *l.c.*, 15–18), and the Malaria Commission of the League of Nations proposed in 1931 that the name quinetum should be restricted to a mixture in equal parts of quinine, cinchonine, and cinchonidine. This standard is recognised in the "British Pharmaceutical Codex," 1934, which requires that quinetum shall contain not less than 60% of quinine and cinchonidine as determined by the "British Pharmacopœia" method for totaquina (*see* p. 132). The loss in drying is not to exceed 5%, and the ash must be 1% or less.

Quinicine.—*See* Quinotoxine, *under* Quinine.

Quinidine (conquinine), $C_{20}H_{24}O_2N_2$, is a naturally occurring dextrorotatory stereoisomeride of quinine, and is stereochemically identical with cinchonine, except that it contains a methoxyl group in the 6-position of the quinoline nucleus. It is found in small quantity in most cinchona barks, but especially in *C. pitayensis*, *C. amygdalifolia*, and *C. Calisaya*. Quinidine is now extracted on a commercial scale, but at one time it was said to be precipitated together with the amorphous alkaloids in the "tails" of quinine manufacture, and so passed into the agglomeration of alkaloids termed by Sertürner "quinoidine" (1828). It was from this source that Henry and Delondre (1833) prepared an alkaloid which they termed "quinidine," while Van Heyningen (1849) also isolated a crystalline alkaloid, isomeric with quinine, but called it "β-quinine," for Winckler (1847) had in the meantime used the name "quinidine" for another alkaloid. Pasteur (1853) renamed Winckler's alkaloid "cinchonidine" (the name which it now bears, *q.v.*), and reverted to Henry and Delondre's original name for the alkaloid here in question, which he isolated also from commercial cinchonine, and which de Vrij (1857) showed to be identical with Van Heyningen's β-quinine. To avoid confusion with Winckler's alkaloid (cinchonidine), Hesse (1865) proposed for the quinidine, now of unambiguous identity, the name "conquinine," a name much used in Germany but not elsewhere. The alkaloid is now almost everywhere known as quinidine.

Quinidine is prepared from quinine sulphate mother-liquors, from which, on adding caustic soda, it passes together with cinchonidine into ether. The cinchonidine is removed as tartrate, and the quinidine isolated as hydriodide. It is the least soluble of the cinchona hydriodides. The base is finally recovered, and recrystallised from alcohol. Quinidine so prepared contains large amounts (*e.g.* 30%) of hydroquinidine which can be removed either by Thron and Dirscherl's mercuric acetate process (Annalen, 1935, **515**, 252), or by fractional recrystallisation of the dihydrochloride from water (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 434).

According to Hesse (Ber. 1877, **10**, 2154; *cf.* Mylius, *ibid.* 1886, **19**, 1773) quinidine crystallises from dilute alcohol in prisms containing $2{\cdot}5H_2O$ (losing $0{\cdot}5H_2O$ on exposure); from absolute alcohol it separates with 1 EtOH; from ordinary ether in rhombohedra containing $2H_2O$; from absolute ether with $\tfrac{1}{3}Et_2O$; from boiling water in leaflets with $1{\cdot}5H_2O$; and from benzene it crystallises in anhydrous needles, m.p. 172°. The quinidine of the "British Pharmaceutical Codex," 1934, 872, contains $2H_2O$ and melts at about 168°. The published rotations of quinidine are: +262° ($c=2$ in alcohol) (Hille, Arch. Pharm. 1903, **241**, 77); +256° ($c=3{\cdot}2$ in alcohol) (Oudemans, Annalen, 1876, **182**, 45); +243·5° ($c=0{\cdot}77$ in alcohol) (Rabe, *ibid.* 1910, **373**, 100); +230° ($c=1{\cdot}8$ in chloroform) (Hesse, *ibid.* 1875, **176**, 224) and +334·2° ($c=0{\cdot}81$, *i.e.* an $M/40$ solution in $0{\cdot}1N$-H_2SO_4) (Buttle *et al. l.c.*). For other rotations, *see* Oudemans (*l.c.*) and Lenz (Z. anal. Chem. 1888, **27**, 571). Quinidine is not very readily soluble in any one organic solvent; it dissolves best in alcohol, but is soluble also in ether, chloroform, benzene or ethyl acetate; it is almost insoluble in cold water, but dissolves in 750 parts of boiling water. It gives the thalleioquin reaction, and exhibits a blue fluorescence in dilute sulphuric acid. Quinidine closely resembles quinine both in chemical and pharmacological properties; both yield the same toxine, quinone, quininic acid, and meroquinene; on oxidation with potassium permanganate it gives rise to quitenidine (*see below*) and on catalytic hydrogenation to hydroquinidine (*q.v.*). On heating with mineral acids it undergoes various changes, *iso*- and *apo*quinidine and their cogeners being formed (*see below*). Quinidine is not greatly inferior to quinine in antimalarial efficacy. It has been recommended for use in place of the lævorotatory quinine in cases of "quinine idiosyncrasy"

Quinidine Hydrochloride, $B\cdot HCl$, crystallises in asbestos-like prisms containing $1H_2O$ (Hesse, Annalen, 1868, **146**, 362; 1875, **176**, 225), $[\alpha]_D$ +205·8° (4·928*c* in water), +212° (2·562*c* in 97% alcohol). The anhydrous salt melts at 258°–259°. It is readily soluble in alcohol or hot water, but only in 62·5 parts of water at 10°. It dissolves also in chloroform, but is almost insoluble in ether.

Quinidine Sulphate, $B_2\cdot H_2SO_4$, crystallises from hot water in prisms with $2H_2O$ (Hesse, Annalen, 1868, **146**, 364; 1875, **176**, 226; 1876, **182**, 141). It is described in "British Pharmacopœia," 1932, 364, as colourless, needle-like crystals. It has $[\alpha]_D$ +179·5° (*c*=1 in water), +211·5° (*c*=2 in alcohol), or +184·2° (*c*=3 of anhydrous salt in chloroform). It is soluble in about 100 parts of cold water, 7 parts of boiling water, 10 parts of alcohol, or 20 of chloroform. It is almost insoluble in ether. The anhydrous salt reabsorbs $2H_2O$ on exposure and is light-sensitive. The acid sulphate is readily soluble in water.

Quinidine Hydriodide, $B\cdot HI$, is precipitated as a crystalline powder when a solution of a quinidine salt is treated with potassium iodide. It is used for the isolation and estimation of quinidine, being very sparingly soluble in cold water (1 in about 1,250) and also in alcohol or boiling water.

The *neutral tartrate*, $B_2\cdot C_4H_6O_6,H_2O$, dissolves in about 40 parts of water, the *acid tartrate* $B\cdot C_4H_6O_6,3H_2O$ (m.p. 100°) in 400 parts.

Quinidine Methiodide,

$$CH_3O\cdot C_9H_5N\cdot CH(OH)\cdot C_7H_{11}N(CH_3I)\cdot CH{:}CH_2,$$

is formed from the components in the cold, or more readily on boiling in alcoholic solution in the dark. It crystallises in colourless needles with $1H_2O$, and is readily soluble in alcohol or boiling water, but sparingly so in cold water. The anhydrous methiodide has m.p. 248° (Claus, Annalen, 1892, **269**, 232). The anhydrous *ethiodide* is similar and has the same m.p. The *dimethiodide*,

$$CH_3O\text{-}C_9H_5N(CH_3I)\text{-}CH(OH)\text{-}C_7H_{11}N(CH_3I)\text{-}CH{=}CH_2,$$

crystallises in yellow rhombic plates with $1\cdot 5H_2O$, m.p. 156°. It is more readily soluble in water, but less readily so in alcohol than the monomethiodide.

Acetylquinidine,

$$CH_3O\text{-}C_9H_5N\text{-}CH(O\text{-}CO\text{-}CH_3)\text{-}C_7H_{11}N\text{-}CH{=}CH_2,$$

is formed on warming quinidine with acetic anhydride at 60°–80°. It is an amorphous powder readily soluble in ether (Hesse, Annalen, 1880, **205**, 318).

a-Chlorohydroquinidine,

$$CH_3O\text{—}C_9H_5N\text{—}CH(OH)\text{—}C_7H_{11}N\text{—}CHCl\text{—}CH_3,$$

is isolated as the dihydrobromide from the products of the reaction of concentrated hydrochloric acid and quinidine (Goodson, J.C.S. 1935, 1097). The base crystallises in needles with $2H_2O$ from 70% alcohol. The anhydrous base has m.p. 206°, *decomp.* 225°, $[\alpha]_D^{24}$ +276·3° (*c*=0·5 in *N*-HCl). The dihydrobromide has m.p. 253°, $[\alpha]_D$ +200° in water.

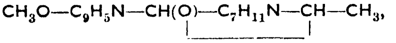
The mother-liquors from the crude dihydrobromide contain *a′-chlorohydroquinidine*, isolated as the neutral tartrate. The base crystallises from dilute alcohol in needles with $3H_2O$. The anhydrous base has m.p. 200°, *decomp.* 229°, $[\alpha]_D^{22}$ + 240·7° (*c*=0·5 in *N*-HCl). The tartrate, $B_2\cdot C_4H_6O_6,11H_2O$, crystallises from 30% alcohol, and when dried sinters at 152° and froths at 196° (Goodson, *l.c.*).

Iodohydroquinidine, better iododihydroquinidine (hydroiodoquinidine),

$$CH_3O\text{—}C_9H_5N\text{—}CH(OH)\text{—}C_7H_{11}N\text{—}CHI\text{—}CH_3.$$

The dihydriodide, $B\cdot 2HI$ (known in the early literature as "trihydriodoquinidine") is formed when quinidine is warmed with hydriodic acid (Schubert and Skraup), Monatsh. 1891, **12**, 669; Lippmann and Fleissner, *ibid.* 1892, **13**, 433), and has m.p. 230°. The base liberated by means of ammonia crystallises from alcohol in prisms, and has m.p. 205°–206°.

a-iso*Quinidine*,



$$CH_3O\text{—}C_9H_5N\text{—}CH(O)\text{—}C_7H_{11}N\text{—}CH\text{—}CH_3,$$

is formed when quinidine is warmed with strong hydrobromic or hydrochloric acid for 50 hours, and the product boiled with alcoholic potash (Domański and Suszko, Bull. Acad. Polonaise, A. 1933, 119). It separates from aqueous acetone with $1H_2O$ and melts at about 80°. The anhydrous base (from dry acetone) melts at 133° and has $[\alpha]_D$ +111° in alcohol. It gives the fluorescence and thalleioquin tests, and on heating with sulphuric acid gives rise to *β-iso*-quinidine. The *hydrochloride* has m.p. 224°.

β-iso*Quinidine*, *isoapo*quinidine (*β-iso*cupreidine) methyl ether, is a stereoisomeride of the preceding substance, and is formed when quinidine, *a-iso*- or *γ-iso*quinidine is heated with moderately concentrated sulphuric acid or by methylating *isoapo*quinidine (*β-iso*cupreidine) (Pfannl, Monatsh. 1911, **32**, 241; Paneth, *ibid.* 257; Konopnicki and Suszko, Bull. Acad. Polonaise, A. 1929, 340; Henry, Solomon and Gibbs, J.C.S. 1935, 966). It crystallises from moist ether or from dilute alcohol with $3H_2O$, m.p. 72°. The anhydrous base has m.p. 142°. $[\alpha]_D$ −9·7° in alcohol, or +29° in 0·1*N*-H_2SO_4. The *neutral sulphate*, $B_2\cdot H_2SO_4,7H_2O$, has $[\alpha]_D$ −47·1° in water (when dehydrated) (Henry *et al.*), or −35·5° (as hydrate) Pfannl).

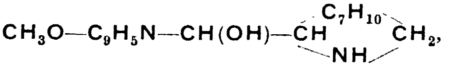
γ-iso*Quinidine* is a stereoisomeride of the two preceding substances, and is formed along with *a-iso*quinidine and with niquidine when quinidine is warmed with strong hydrobromic or hydrochloric acid for 50 hours, and the product boiled with alcoholic potash (Domański and Suszko, Rec. trav. chim. 1935, **54**, 481). It crystallises from aqueous acetone with $2H_2O$, m.p. about 70°. The anhydrous base, which cannot be crystallised, has $[\alpha]_D$ +51·1° in alcohol. The acid nitrate has m.p. 196° and the hydriodide, m.p. 180°–183°.

*Methyl*apo*quinidine*,

$$CH_3O—C_9H_5N—CH(OH)—C_6H_{10}N{>}C=CH—CH_3,$$

an isomeride of the preceding three substances, is formed together with β-*iso*quinidine when quinidine is heated with 60% sulphuric acid, or by methylating *apo*quinidine (Henry, Solomon and Gibbs, J.C.S. 1935, 966). It separates from ether or alcohol in anhydrous crystals, m.p. 185°, $[\alpha]_D^{15}$ +278° in $0{\cdot}1N$-H_2SO_4, or +193·2° in alcohol. From aqueous acetone it crystallises with $1\frac{1}{2}H_2O$, m.p. about 90°. The *hydrochloride* $B{\cdot}HCl,H_2O$, crystallises from water or alcohol; the anhydrous salt has m.p. 267°, $[\alpha]_D$ +174·7° in water. The geometrical isomeride of this substance, neoiso*quinidine*, crystallises from ether with $2H_2O$; it has m.p. 83°, and $[\alpha]_D$ +198·6° in dil. H_2SO_4 or +98·7° in alcohol (Henry, Solomon and Gibbs, *ibid.* 1937, 596).

Niquidine (Domański and Suszko, Bull. Acad. Polonaise, A. 1935, 457) is claimed to be isomeric with quinidine, and to have the partial structure



$$CH_3O—C_9H_5N—CH(OH)—\overset{\displaystyle C_7H_{10}}{\underset{\displaystyle NH}{CH\quad CH_2}},$$

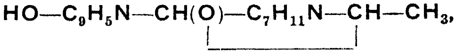
in which the quinuclidine bridge has undergone rupture. It is also claimed to be an analogue of niquine (*see under* Quinine) the composition of which is still in dispute. Niquidine occurs along with α- and γ-*iso*quinidine when the halogenohydroquinidines are dehalogenated with alcoholic potash. It crystallises from acetone, m.p. 161°, $[\alpha]_D$ +171° in alcohol. The acid oxalate has m.p. 206°–207° and the dihydrobromide, m.p. 250°. It has a secondary nitrogen atom and forms N-acetyl and diacetyl derivatives.

apo*Quinidine*,

$$HO—C_9H_5N—CH(OH)—C_6H_{10}N=C{>}CH—CH_3,$$

is one of the phenolic products formed when quinidine is demethylated with boiling 60% sulphuric acid (Henry, Solomon and Gibbs, J.C.S. 1935, 966). It is soluble in sodium hydroxide solution, from which it is precipitated again by carbon dioxide. It crystallises from alcohol with $1EtOH$ (m.p. 172°) or from acetone with $1Me_2CO$ (m.p. 178°–180°), and these can only be removed at 150°–160°. The anhydrous base has m.p. 185°–190° and $[\alpha]_D$ +291·4° in dil. H_2SO_4 or +208·6° in alcohol (figures calc. for anhydrous base from measurements on the alcoholate). The *hydrochloride*, $B{\cdot}HCl$, which is yellow in aqueous solution, crystallises from alcohol with $1EtOH$ (m.p. 183°–185°) which is replaced by $2H_2O$ on exposure to air (m.p. 235°), but which is not expelled on drying at 120°. The dihydrate of this salt is also obtained by crystallisation from water: $1H_2O$ is readily expelled at 120°, the other is more tenaciously retained. The geometrical isomeride of this substance, neoapo*quinidine*, crystallises from ether or alcohol, m.p. 260°, $[\alpha]_D$ +206·2° in dil. H_2SO_4 or +120·7° in alcohol (Henry, Solomon, and Gibbs, *ibid.* 1937, 595).

isoapo*Quinidine* (β-*iso*cupreidine),



$$HO—C_9H_5N—CH(\underline{O)—C_7H_{11}N—CH}—CH_3,$$

is formed along with *apo*quinidine when quinidine or β-*iso*quinidine is demethylated by boiling with 60% sulphuric acid (Henry and Solomon, J.C.S. 1934, 1923; Ludwiczak and Suszko, Bull. Acad. Polonaise, A, 1935, 65). It is a phenolic base soluble in alkali, and on methylation affords β-*iso*quinidine. It crystallises from alcohol, has m.p. 245° and $[\alpha]_D$ −12·6° in alcohol, or +25·6° in $0{\cdot}1N$-H_2SO_4. The *hydrochloride* has m.p. 255° and is yellow in aqueous solution.

Apart from *apo*- and *isoapo*quinidine, Ludwiczakówna, Suszko and Zwierzchowski (Rec. trav. chim. 1933, **52**, 847) find also " cupreidine " among the products obtained by the demethylation of " quinidine " with boiling 60% sulphuric acid. The new phenolic base is claimed to bear the same stereo-chemical relation to cupreine as quinidine bears to quinine, *i.e.* that it is the phenol corresponding to quinidine, and quinidine is said to be regenerated from it on methylation. The possibility, however, of such demethylation without simultaneous isomerisation has been questioned (Henry and Solomon, J.C.S. 1934, 1923; Thron and Dirscherl, Annalen, 1935, **515**, 252), and it has been made probable that the Polish workers' " cupreidine " is hydrocupreidine derived from the hydroquinine which may be present to the extent of about 20% in commercial quinidine.

epi*Quinidine*, $C_{20}H_{24}O_2N_2$, is epimeric with quinidine about the carbinol ($CH{\cdot}OH$) group. It occurs naturally and can be isolated from " quinoidine " (the residues from quinine manufacture) (Dirscherl and Thron, Annalen, 1935, **521**, 48), but is best obtained by epimerisation of quinine or quinidine by boiling with amyl alcoholic potassium hydroxide. There is formed a mixture in dynamic equilibrium of quinine, quinidine, *epi*quinine, and *epi*quinidine. The quinine being removed as neutral tartrate, and the quinidine as acid tartrate, the two *epi*-bases are isolated as dihydrochlorides; the *epi*quinine is then removed as the sparingly soluble dibenzoyltartrate. The residual *epi*quinidine dibenzoyltartrate is purified by recrystallisation. The base crystallises from ether in glistening leaflets, m.p. 113°, $[\alpha]_D^{19}$ +102·4° (c=0·8648 in alcohol). It is very readily soluble in alcohol, but less so in ether. It is more strongly fluorescent than either quinine or quinidine. The *dibenzoyltartrate* has m.p. 167°, and the *dihydrochloride*, m.p. 195°–196° (Rabe and others, Annalen, 1932, **492**, 252, 258–261).

Quinidine Chloride,

$$CH_3O—C_9H_5N—CHCl—C_7H_{11}N—CH=CH_2,$$

is prepared by treating dry quinidine hydrochloride in chloroform with phosphorus pentachloride (Comstock and Koenigs, Ber. 1885, **18**, 1223; Rabe, Annalen, 1910, **373**, 104). It crystallises from ether or a mixture of ether and benzene, m.p. 131°–132°, $[\alpha]_D^{15}$ +35·25° (c=1·943 in alcohol). It dissolves readily in alcohol, benzene or chloroform fairly sparingly in dry ether, and very sparingly in light petroleum. The *hydrochloride* (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1501) crystallises from a mixture of absolute alcohol and a little dry ether in cream-coloured, woolly needles, m.p. 199°–206°, $[\alpha]_D^{25}$ +47·7° ($c=1·017$ in water). It is readily soluble in water or methyl alcohol, less readily so in chloroform and almost insoluble in acetone.

Desoxyquinidine,

$$CH_3O—C_9H_5N—CH_2—C_7H_{11}N—CH{=}CH_2$$

is prepared by reducing a dilute sulphuric acid soltuion of quinidine chloride with iron filings (Koenigs, Ber. 1895, **28**, 3147; Rabe, Annalen, 1910, **373**, 107; Giemsa and Halberkann, Ber. 1921, **54**, 1200). It separates from ether or from aqueous acetone or alcohol with $2H_2O$, m.p. 80°–82°, $[\alpha]_D^{20}$ for anhydrous base in alcohol +211° (Rabe) or +194° (Giemsa and Halberkann). It shows an intense violet fluorescence in tartaric acid as well as in alcoholic solution. The *hydrochloride* (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1501) crystallises from a mixture of alcohol and ether with the equivalent of $1\,H_2O$, m.p. *indef.* 125°–145° (*dry*), and $[\alpha]_D^{30°}$ +82° in water (*dry*). The salt is readily soluble in water, alcohol, or chloroform, fairly readily in hot acetone and somewhat also in benzene. Desoxyquinidine, which closely resembles quinene (*q.v., under* Quinine), is characterised by the ready solubility of its acid tartrate.

Quitenidine,

$$CH_3O—C_9H_5N—CH(OH)—C_7H_{11}N—CO_2H,$$

is obtained by the oxidation of quinidine in sulphuric acid solution at 0° with potassium permanganate (Forst and Böhringer, Ber. 1882, **15**, 1659). It crystallises from hot water or from dilute alcohol in leaflets with $2H_2O$, m.p. 240°–246° (*decomp.*), $[\alpha]_D^{23}$ +258° ($c=5$ of anhydrous substance in N-H_2SO_4) (Goodson, Henry, and Macfie, Biochem. J. 1930, **24**, 881). It is soluble in 200 parts of cold water, but more readily in hot water and very sparingly in alcohol. As an acid it is soluble in alkalis; it shows the thalleioquin reaction and a blue fluorescence in dilute sulphuric acid solution. The acid sulphate, $B·H_2SO_4,3H_2O$, crystallises from dilute alcohol.

epiQuinidine.—*See under* Quinidine.

Quinine, $C_{20}H_{24}O_2N_2$, is the most important of the cinchona alkaloids. It was first isolated by Pelletier and Caventou (Ann. Chim. 1820, **15**, 348) from the "cinchonino" of Gomes (1810), a crystalline mixture of alkaloids obtained from Vauquelin's "quina" (1809); the latter was an amorphous extract of cinchona bark, and had been first prepared by Fourcroy in 1792. Quinine occurs in all genuine cinchona barks, and particularly in *Calisaya* bark, the cultivated descendant of which, *C. Ledgeriana*, being made to yield as much as 8% of quinine. For an account of the occurrence of quinine, of the cultivation and commercial history of cinchona plantations, of the extraction, preparation, estimation, and detection of quinine, as well as of the detection of impurities therein, the reader is directed to the first three sections of this article.

The quinine of commerce usually contains cinchonidine and hydroquinine as impurities. These are readily removed by recrystallisation of the sulphate, acid sulphate, dihydrobromide, *d*-camphorsulphonate, or *d*-bromocamphorsulphonate, or by regeneration of the base from the periodide known as *herapathite* (*see* Hesse, Pharm. J. 1884, **15**, 869; 1885, **16**, 358, 818; 1886, **17**, 585; Tutin, *ibid.* 1909, **83**, 600; Emde, Helv. Chim. Acta, 1932, **15**, 574; Buttle, Henry, and Trevan, Biochem. J. 1934, **28**, 433). Hydroquinine may also be removed by the mercuric acetate process of Thron and Dirscherl (Annalen, 1935, **515**, 252).

The percentage composition of quinine ($C_{10}H_{12}ON$) was first correctly determined by Liebig (1838); the empirical formula

$$C_{20}H_{24}O_2N_2$$

assigned to it the same year by Regnault was not established until 1854, when Strecker confirmed it by analyses of quinine alkyliodides (Annalen, 1854, **91**, 155). For the constitution of quinine and other cinchona alkaloids, *v.* section 5 (p. 137) of this article.

Quinine base is precipitated from aqueous acid solutions of its salts at first as a white, anhydrous, amorphous powder. To avoid precipitating the frequently sparingly soluble neutral salts (particularly, for example, the sulphate:

$$2(B·H_2SO_4)+2NaOH$$
$$=B_2·H_2SO_4+Na_2SO_4+2H_2O),$$

this operation is best performed by introducing the alkaloidal solution very slowly *into* a large excess of the well-stirred solution of the alkali. When ammonia is used as the precipitating agent, the amorphous base gradually turns into a crystalline efflorescent trihydrate, $B·3H_2O$, m.p. 57°. $1\,H_2O$ is lost on drying in the air, so that the article of commerce is usually $B·2H_2O$; the other two water molecules are removed over concentrated sulphuric acid or on drying in an oven. The anhydrous base can also be obtained by crystallisation from hot dilute alcohol, boiling water, or ammonia solution at 100° under pressure, or by precipitating a hot solution of a quinine salt with sodium carbonate or bicarbonate. Quinine separates from benzene in crystals of the composition B,C_6H_6. Anhydrous quinine base has m.p. 173·5°, $[\alpha]_D$ in alcohol −169·3° ($c=2$) (Hesse, Annalen, 1875, **176**, 206), or −167·5° ($c=1·6$) (Oudemans, *ibid.* 1876, **182**, 44), or −158·2° ($c=2·136$) (Rabe, *ibid.* 1910, **373**, 100); $[\alpha]_D$ in chloroform −116° ($c=2$); $[\alpha]_D$ in dilute hydrochloric or sulphuric acid −278° to −279° ($c=1·6$) (Oudemans), or −284·5° ($c=0·8$, *i.e.* an $M/40$ solution) (Buttle, Henry and Trevan, Biochem. J. 1934, **28**, 436). One part of quinine requires for solution nearly 2,000 parts of cold water, but dissolves in about 1,000 parts of boiling water; the presence of fixed alkalis lowers the solubility, but ammonia augments it, supersaturated solutions being readily formed. Quinine dissolves in less than its own volume of alcohol; in ether its solubility depends greatly on the quality of the solvent, and widely varying figures have been published (1 in 4·5 to 1 in 114); it is more soluble in wet ether than in the dry solvent, and, as with ammonia, readily forms supersaturated solutions, which may account for some of the high solubilities recorded. On evaporation, ethereal solutions leave a residue consisting of a resinoid mass. Quinine is very soluble also in chloroform (1 in 2 parts), but requires nearly 200 parts of carbon tetrachloride. It is fairly soluble in ethyl acetate, sparingly in cold but fairly readily in hot benzene, and is almost insoluble in light petroleum (b.p. 60°) (1 in 5,000 parts). Dilute solutions of quinine in dilute sulphuric and other oxy-acids exhibit a blue fluorescence, which is weakened and may even be destroyed by the addition of halides, ferrocyanides, or thiosulphates. This property enables one part of quinine to be detected in several hundred thousand parts of water. The thalleioquin reaction is not quite so delicate; a faintly acid solution of quinine is treated with chlorine or bromine water drop by drop until there is a slight excess of the halogen (bleaching powder is sometimes used), when on addition of an excess of dilute ammonia solution, a rich emerald green coloration or precipitate is produced.

Quinine undergoes a variety of chemical reactions; the products are described in greater detail below. On heating with dilute organic acids, or on melting certain salts, or on heating them in glycerol, quinotoxine (quinicine) is formed; with mineral acids quinine undergoes isomerisation to *iso*quinine, and also simultaneous demethylation, *apo*quinine and other phenolic substances being formed. Potassium permanganate oxidises it to quitenine, and chromic acid to quininic acid and to meroquinene and its oxidation products (*see under* Cinchonine). On catalytic hydrogenation it gives rise to hydroquinine.

Quinine Sulphate, $B_2\cdot H_2SO_4$, crystallises from boiling water probably with $8H_2O$. Being very efflorescent, however, the water content is difficult to determine with accuracy, and is often given as 7 and $7{\cdot}5H_2O$. The latter hydrate is official in the "British Pharmacopœia," 1932 (p. 370). The salt, the appearance of which is influenced by impurities, forms a light mass of colourless, odourless, glistening silky needles, of intensely bitter taste. They rapidy effloresce on exposure or on warming at 50° with the formation of lustreless crystals, $B_2\cdot H_2SO_4,2H_2O$, which constitutes the stable form, and is formed also from the anhydrous salt on exposure. The anhydrous salt, which can be obtained by drying at 100°, has $[\alpha]_D$ −235° (c=1 in dil. H_2SO_4) (Tutin, Pharm. J. 1909, **83**, 603). The salt with $7{\cdot}5H_2O$ requires for solution nearly 800 parts of cold water, but dissolves in 30 parts of boiling water. It is soluble in 65 parts of cold 90% alcohol, less soluble in absolute alcohol, and very soluble in hot 90% alcohol. It also dissolves in 30 parts of glycerol, but hardly at all in ether or chloroform, although in a mixture of the latter with alcohol it is more soluble than in either solvent alone. Quinine sulphate is faintly alkaline to litmus, and on exposure to light slowly turns yellow.

Quinine Acid Sulphate (bisulphate),

$$B\cdot H_2SO_4,7H_2O,$$

crystallises from water in small, colourless, transparent or opaque, acicular crystals. It is odourless, but intensely bitter. The salt is efflorescent and light-sensitive. Aqueous solutions are fluorescent, and acid to litmus, but not to Congo red. The anhydrous salt has m.p. 160° (*decomp.*) and $[\alpha]_D^{15}$ −211·7° (c=1·06, *i.e.* an $M/40$ solution in water). It is soluble in about 10 parts of cold water or 20 of alcohol, but is much more soluble at higher temperatures. The "*tetrasulphate*," $B\cdot 2H_2SO_4$, crystallises from water with $7H_2O$ or from alcohol with $5H_2O$. It is very soluble in water, less so in alcohol.

Quinine Hydrochloride, $B\cdot HCl,2H_2O$, forms colourless glistening needles, which are efflorescent in warm or dry air. The anhydrous salt has m.p. 158°–160°, and $[\alpha]_D$ −155·8° in water, and about the same rotation in alcohol. It is remarkable in having a greatly diminished rotation in chloroform (−57° in 1%, and only −21° in 9% solution). The solubility of this salt in water is given variously between 2·5 and 6%; it is very soluble in alcohol, chloroform, or boiling water. The *dihydrochloride*, $B\cdot 2HCl$, forms a white crystalline powder, m.p. 180°–185° (*decomp.*), very soluble in water, less so in alcohol.

Quinine Hydrobromide, $B\cdot HBr$, crystallises with $1H_2O$ according to Hesse (Chem. Zentr. 1902, ii, 953), but with $2H_2O$ according to the "British Pharmaceutical Codex," 1934, 887. It is soluble in 55 parts of cold water, but is readily soluble in alcohol, chloroform, or boiling water. The *dihydrobromide*, $B\cdot 2HBr,3H_2O$, is very soluble in water or alcohol.

A very large number of other salts, derivatives and preparations of quinine, are known; only a small selection, however, can be given here of those that are available for use in medicine.

Quinine and Urea Hydrochloride,

$$B\cdot HCl\cdot CO(NH_2)_2\cdot HCl,5H_2O,$$

is prepared by dissolving a molecular proportion of urea (60 parts) in a solution of quinine hydrochloride (400 parts) in 300 parts hydrochloric acid (sp.gr. 1·05). The salt having the above composition crystallises out. It has m.p. 72° and is soluble in one part of water and two parts of alcohol. It is acid to litmus in aqueous solution, and gives the fluorescence and thalleioquin reactions characteristic of quinine. A similar preparation is quinine and urethane hydrochloride, usually prepared as a solution for injection ("British Pharmaceutical Codex," 1934, pp. 889, 1287).

Quinine Acetylsalicylate, $B\cdot C_9H_8O_4$, prepared by mixing alcoholic solutions of the components, is a white crystalline powder, m.p. about 160°, soluble in 330 parts of water, or 50 of alcohol.

Quinine Citrate, $B_3\cdot C_6H_8O_7,7{\cdot}5H_2O$, or $B_2\cdot C_6H_8O_7,7H_2O$, white needles, soluble in about 1,000 parts of water.

Quinine Disalicylosalicylate or bisalicylosalicylate (" quinisal," " quinisan "),

$$B\cdot 2(C_7H_5O_3—C_7H_5O_2),$$

is prepared by mixing quinine acid sulphate and sodium salicylosalicylate in aqueous solution. It is described as a white microcrystalline powder having only a slightly bitter taste, insoluble in water and very soluble in alcohol.

Quinine Formate (" quinoform "), $B\cdot CH_2O_2$, consists of crystals, m.p. about 130°, fairly soluble in water.

Quinine Glycerophosphate (" kineurine "), $B_2\cdot C_3H_7O_3\cdot H_2PO_3,4H_2O$, from quinine hydrochloride and calcium glycerophosphate, occurs in crystals, m.p. 154°, soluble in 200 parts of water. It is bitter.

Quinine Hypophosphite, $B\cdot H_3PO_2,2H_2O$, is a crystalline or amorphous powder fairly readily soluble in water.

Quinine Iodobismuthate, $(BiI_3)_2\cdot B\cdot 2HI$, a red amorphous powder prepared by mixing solutions of quinine hydrochloride, bismuth chloride, potassium iodide, and hydrochloric acid (François and Séguin, J. Pharm. Chim. 1925, **2**, 59).

Quinine Phosphate, $B_3\cdot 2H_3PO_4,6H_2O$, or $B_2\cdot H_3PO_4,8H_2O$, occurs in needles which resemble quinine sulphate both in appearance and solubility.

Quinine Salicylate, $B\cdot C_7H_6O_3,H_2O$, from quinine sulphate and sodium salicylate in aqueous solution. It occurs in white silky needles, very sparingly soluble in water.

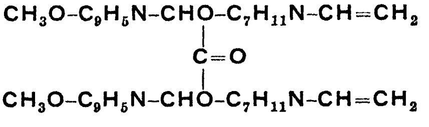
Quinine Tannate is prepared by mixing solutions of quinine sulphate and tannic acid in the presence of ammonia. It is a pale yellow, amorphous powder, having an astringent, barely bitter taste. It is slightly soluble and only slowly absorbed.

Quinine Valerate (valerianate),

$$B\cdot C_5H_{10}O_2\cdot H_2O,$$

consists of colourless, lustrous, pearly crystals, or of a white, micro-crystalline powder, m.p. about 90°, slightly soluble in water, and having a bitter taste and a faint odour of valeric acid.

Quinine Carbonate (diquinine carbonate, " aristochin "),



$$\begin{array}{c}CH_3O-C_9H_5N-CHO-C_7H_{11}N-CH=CH_2\\ |\\ C=O\\ |\\ CH_3O-C_9H_5N-CHO-C_7H_{11}N-CH=CH_2\end{array}$$

is a tasteless, amorphous, insoluble powder, m.p. 189°, made by treating quinine with phosgene in benzene solution.

Quinine Ethylcarbonate (" British Pharmacopœia," 1932),

$$CH_3O-C_9H_5N-CH(O-CO-OC_2H_5)-C_7H_{11}N-CH=CH_2,$$

occurs in white, almost tasteless, needles, m.p. about 90°, slightly soluble in water. It is made by treating quinine with chloroformic ester ($Cl\cdot CO_2C_2H_5$) in benzene solution.

The following are the principal derivatives, transformation, and degradation products of quinine, which at present are only of academic interest:

Acetylquinine,

$$CH_3O-C_9H_5N-CH(O-CO-CH_3)-C_7H_{11}N-CH=CH_2,$$

was first prepared by Hesse (Annalen, 1880, **205**, 317; *cf.* Beckett and Wright, J.C.S. 1876, **29**, 657) by warming quinine with acetic anhydride. Other methods have been patented by Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H. (G.P. 128116/1902, 178172, 178173/1906). It crystallises from ether in prisms, m.p. 108°, or from light petroleum, m.p. 116°–117°, has $[\alpha]_D$ −54·3° in alcohol, or −114·8° in dilute acid, and is readily soluble in alcohol, ether or chloroform. It is almost tasteless and can be hydrolysed back to quinine.

Benzoylquinine,

$$CH_3O—C_9H_5N—CH(O-CO-C_6H_5)-C_7H_{11}N-CH=CH_2,$$

was first made by Schützenberger (Annalen, 1858, **108**, 352; *cf.* Wunsch, Ann. Chim. 1896, [vii], **7**, 127) by the action of excess of benzoyl chloride on quinine on the water bath. Other methods have been patented by Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H. (G.P. 128116/1900, 178172, 178173/1905). It crystallises from ether, m.p. 139°, $[\alpha]_D$ +121·6° in alcohol, and forms a *hydrochloride*,

$$B\cdot HCl,\tfrac{1}{2}H_2O,$$

which when dry has m.p. 226°.

Quinine Methiodide,

$$CH_3O\cdot C_9H_5N\cdot CH(OH)\cdot C_7H_{11}N(CH_3I)\cdot CH:CH_2,$$

is obtained when equimolecular proportions of the components react in ethereal or alcoholic solution in the cold (Claus and Mallmann, Ber. 1881, **14**, 76; Hesse, *ibid.* 1895, **28**, 1298). It crystallises from water in colourless needles, with 1 or $2H_2O$, m.p. 233°–236° (*decomp.*), is very sparingly soluble in ether or chloroform, sparingly in cold water, but readily so in alcohol. The *dimethiodide*,

$$CH_3O\cdot C_9H_5N(CH_3I)\cdot CH(OH)\cdot C_7H_{11}N(CH_3I)\cdot CH:CH_2,$$

is formed from it (also from cupreine and from quinine) by boiling with an excess of methyl iodide in alcoholic solution. It crystallises from water in yellow plates with $3H_2O$, m.p. about 160° (*decomp.*).

Quinine Ethiodide,

$$CH_3O\cdot C_9H_5N\cdot CH(OH)\cdot C_7H_{11}N\cdot(C_2H_5I)\cdot CH:CH_2,$$

crystallises from water with $1H_2O$. The anhydrous substance has m.p. 210°–211° and $[\alpha]_D$ −105° in alcohol. It is readily soluble in alcohol, but sparingly so in cold water.

Isomeric *Quinine Ethiodide*,

$$CH_3O\cdot C_9H_5N(C_2H_5I)\cdot CH(OH)\cdot C_7H_{11}N\cdot CH:CH_2,$$

(Skraup and von Norwall, Monatsh. 1894, **15**, 47) is obtained as the hydriodide (m.p. 234°, *dry*) by heating quinine hydriodide with ethyl iodide in alcoholic solution at 100° (sealed tube). It crystallises from 50% alcohol in needles with $3H_2O$, m.p. 93°, and is very soluble in alcohol, but sparingly so in water.

Quinine Diethiodide,

$$CH_3O\cdot C_9H_5N(C_2H_5I)\cdot CH(OH)\cdot C_7H_{11}N(C_2H_5I)\cdot CH:CH_2$$

prepared from either of the two preceding substances by boiling with ethyl iodide in alcoholic solution, crystallises with $1H_2O$, m.p. 157°–160°.

α-Chlorohydroquinine, better, α-chlorodihydroquinine (component of " hydrochloroquinine "),

$$CH_3O{\cdot}C_9H_5N{\cdot}CH(OH){\cdot}C_7H_{11}N{\cdot}CHCl{\cdot}CH_3,$$

is prepared either by leaving quinine hydrochloride to stand in hydrochloric acid (saturated at −17°) for several weeks (Comstock and Koenigs, Ber. 1887, **20**, 2517), or by heating with the ordinary concentrated acid at 85° in a sealed tube (Hesse, Annalen, 1893, **276**, 125). α-Chlorohydroquinine is isolated from the products and purified first as acid nitrate, and then by crystallisation and recrystallisation of the base from methyl alcohol (Goodson, J.C.S. 1935, 1095), when it separates in anhydrous rhombs, m.p. 210°–215° (*decomp.*), $[\alpha]_D^{20}$ −251° (c=0·5 in N-HCl). The *acid nitrate* $B{\cdot}2HNO_3$, has m.p. 212°, and the *tartrate*, $B_2{\cdot}C_4H_6O_6,7H_2O$, 198° (*dry*).

α′-Chlorohydroquinine is epimeric with the preceding substance at the carbon atom which carries the chlorine atom. It is formed along with it, the mixture constituting " hydrochloroquinine " (Goodson, *l.c.*). It is found in the mother-liquors from the methyl alcoholic crystallisation of the bases, whence it is isolated as acid nitrate, the base recovered, and recrystallised from benzene. It crystallises with solvent of crystallisation, but on exposure to air, the benzene is replaced by water. The anhydrous base has m.p. 194°, *decomp.* 225°, and $[\alpha]_D$ −168·1° (c=0·5 in N-HCl). The *acid nitrate*, $B{\cdot}2HNO_3$, has m.p. 223°, and the *tartrate*, $B_2{\cdot}C_4H_6O_6,2H_2O$, 228° (*dry*).

α-Bromohydroquinine, α-bromodihydroquinine, hydrobromoquinine II (component of " hydrobromoquinine "),

$$CH_3O{\cdot}C_9H_5N{\cdot}CH(OH){\cdot}C_7H_{11}N{\cdot}CHBr{\cdot}CH_3,$$

is prepared by causing quinine dihydrobromide to react with hydrobromic acid (saturated at −17°) at room temperature for 3 days (Comstock and Koenigs, Ber. 1887, **20**, 2518), or by heating quinine hydrochloride with 38% hydrobromic acid in acetic acid at 80° for 2½ hours (Podlewski and Suszko, Rec. trav. chim. 1936, **55**, 392). α-Bromohydroquinine base is isolated from the products by crystallisation from ether, and purified by recrystallisation from acetone, when it separates in the form of prisms, m.p. 166 °–167° (*decomp.*), $[\alpha]_D$ −200° in alcohol-chloroform (1 : 2). With alcoholic potash it gives rise to niquine (*see below*).

α′-Bromohydroquinine (hydrobromoquinine I), epimeric with the preceding substance at the carbon atom which carries the bromine atom (Podlewski and Suszko, *l.c.*), is formed along with it, and is isolated from the ethereal mother-liquors of mixed bromo-bases by recrystallisation from benzene. It separates with one molecule of solvent of crystallisation, has m.p. 160°–162° (*decomp.*), and $[\alpha]_D$ −50° in alcohol-chloroform. With alcoholic potash it gives rise to β-*iso*quinine (*see below*). Its *quarternary metho*-p-*toluene-sulphonate* crystallises from water, m.p. 193°–194°.

α-Iodohydroquinine, α-iododihydroquinine, hydroiodoquinine II (component of " hydroiodoquinine "),

$$CH_3O{-}C_9H_5N{-}CH(OH){-}C_7H_{11}N{-}CHI{-}CH_3,$$

is formed when quinine is heated with hydriodic acid (sp.gr. 1·7) on the water bath for 1 or 2 hours (Lippmann and Fleissner, Monatsh. 1891, **12**, 327, and later papers; Skraup, *ibid.* 431, and later papers). The epimerides formed are isolated as dihydriodides; the bases are then liberated, and separated from one another by crystallisation from benzene and from ether (Rosenmund and Kittler, Arch. Pharm. 1924, **262**, 20; *see also* Reyman and Suszko, Bull. Acad. Polonaise, A, 1935, 360). α-Iodohydroquinine on heating begins to decompose above 100°, and the decomposition reaches a climax at about 150°. The specific rotation is −128° (Rosenmund) or −217° (Reyman and Suszko). On boiling in benzene solution, or on treatment with alcoholic potash, niquine (*see below*) is formed.

α′-Iodohydroquinine, hydroiodoquinine I, is the epimeride of the foregoing compound. According to Rosenmund and Kittler (*l.c.*) it has the same melting-point, but $[\alpha]_D$ −74·3°. According to Reyman and Suszko (*l.c.*), however, it crystallises with one molecule of benzene and melts at 93°, re-solidifies and then decomposes at 130°–140°; it cannot be freed from benzene without decomposition; the crystals containing benzene have $[\alpha]_D$ −18° in alcohol. The methiodide has m.p. 112°–114°. On boiling with benzene, or on treatment with alcoholic silver nitrate or potash, α′-iodohydroquinine gives rise to β-*iso*quinine (*see below*).

The hydroxy-compound corresponding to the above halogen-derivatives is said to be formed when quinine is treated with cold concentrated sulphuric acid, and the resulting sulphonic acid saponified by boiling with dilute sulphuric acid (Vereinigte Chininfabriken, Zimmer & Co., G.m.b.H., G.P. 152174/1904).

By treating quinine with the halogen hydracids and with sulphuric acid under more drastic conditions, there is obtained a series of halogeno-hydro*apo*quinines and a hydroxyhydro*apo*-quinine respectively, differing from the preceding substances only in having a hydroxyl in place of the methoxyl group in the 6-position of the quinoline nucleus. These phenols, however, have not been so fully studied.

*α-iso*Quinine*, *isoapo*quinine methyl ether (component of " *pseudo*quinine "),

$$CH_3O{-}C_9H_5N{-}CH(OH){-}C_8H_{10}N{>}C{=}CH{-}CH_3,$$

is formed in small quantity when quinine is heated with sulphuric acid (sp.gr. 1·61 at 100°) (Böttcher and Horovitz, Monatsh. 1912, **33**, 571), but is probably better obtained by the methylation of *isoapo*quinine. It is isolated from the other products of the reaction as the tartrate, and is purified by recrystallisation of the base from benzene. It has m.p. 196·5°, $[\alpha]_D$ −245° (c=1 in alcohol).

*β-iso*Quinine*, *iso*quinine, *apo*quinine methyl ether (component of " pseudoquinine ") is the geometrical isomeride of the preceding substance. It is formed together with α-*iso*quinine, niquine, and other substances when quinine is heated with sulphuric acid (sp.gr. 1·61) at 100° (Böttcher and Horovitz, *ibid.* 576), when the halogeno-hydroquinines are dehalogenated (*see*, for example, Suszko, Bull. Acad. Polonaise, A, 1925, 129), and when *apo*quinine is methylated (*see*, for example, Henry and Solomon, J.C.S. 1934, 1928; with Gibbs, *ibid.* 1935, 968). In the first two cases it is formed as the principal component of the products, which may contain also unchanged quinine, *a-iso*quinine, niquine, and hydroxyhydroquinine. It is isolated together with the quinine and *a-iso*quinine in the ether-soluble fraction; the quinine and *a-iso*quinine may be removed as the sulphate and tartrate respectively, the *β-iso*quinine being then isolated as the oxalate, and purified by recrystallisation of the base preferably from acetone, but also from dilute alcohol, ether or benzene. It has m.p. 189° (Böttcher), $[\alpha]_D$ −201° in alcohol (Henry) or −192° (−195°) (Böttcher, Suszko), −295·9° in dilute sulphuric acid. The hydrochloride has m.p. 249°–251°, $[\alpha]_D$ −174° in water, and the sulphate, m.p 220°.

Niquine, of disputed composition, the formulæ in question being $C_{19}H_{24}O_2N_2$, $C_{20}H_{24}O_2N_2$, and $C_{20}H_{26}O_2N_2$, is formed when iodo-, or bromohydroquinine is dehalogenated. This may be effected either by treatment with alcoholic potash or alcoholic silver nitrate, or by boiling the *halogeno-bases in benzene solution.* When using the crude mixture of *a*- and *a′*-halogeno formed by the treatment of quinine with halogen hydracids, the dehalogenation gives rise to a mixture of niquine and *β-iso*quinine. It is also said to be formed in minute amount together with *β-iso*quinine, when quinine is treated with sulphuric acid (Giemsa and Oesterlin, Ber. 1931, **64**, [B], 60). Niquine crystallises from boiling water, or dilute alcohol, with $2H_2O$, m.p. about 100°. It is almost insoluble in moist ether. The water is lost in a desiccator and the anhydrous base then melts at 146°, and becomes soluble in dry ether. The anhydrous base has $[\alpha]_D$ −129° in alcohol. It is generally agreed that niquine contains the hydroxyl group of quinine intact; but that the quinuclidine nitrogen atom is changed from tertiary to secondary, because niquine forms a diacetyl-derivative, and a N-nitrosamine. It reacts additively with hydriodic acid, and is largely regenerated from the resulting compound by treatment with alcoholic potash, a small amount of "*iso*niquine" being also formed (Skraup, Monatsh. 1893, **14**, 440; for the remaining literature of niquine, *see* Lippmann and Fleissner, *ibid.* 555; Rosenmund and Kittler, Arch. Pharm. 1924, **262**, 23; Suszko, Bull. Acad. Polonaise, A, 1925, 129; Reyman and Suszko, *ibid.* 1935, 360; Podlewski and Suszko, Rec. trav. chim. 1936, **55**, 392; for constitution by analogy with cinchonhydrine, which will be found under Cinchonine, *see also* references given there).

apo*Quinine*, *β-iso*cupreine,

$$HO—C_9H_5N—CH(OH)—C_8H_{10}N{>}\,C{=}CH—CH_3,$$

is the principal crystalline component of the amorphous mixture obtained when quinine is demethylated or cupreine isomerised with hot dilute mineral acids or with aluminium chloride. The amorphous mixture was first obtained by Hesse (Annalen, 1880, **205**, 323) who, taking it to be a single substance, called it "apoquinine." It is best prepared by boiling quinine with 60% sulphuric acid (Jarzyński, Ludwiczakówna, and Suszko, Rec. trav. chim. 1933, **52**, 841), and can be freed from its congeners by repeated reprecipitation, followed by fractional crystallisation of the acid sulphate or of the dihydrobromide (Henry and Solomon, J.C.S. 1934, 1927). *apo*Quinine, which is persistently amorphous until fairly pure, crystallises from ether, alcohol or acetone, in each case with solvent of crystallisation, which is removed with difficulty, and not without loss of the crystalline state. It froths at 184°, and the froth becomes a clear liquid at about 205°; the anhydrous base has $[\alpha]_D^{20}$ −214·8° (c=0·775 in alcohol), or −281° (c=0·784 in 0·1N-H_2SO_4). *apo*-Quinine is a phenolic substance, soluble in alkalis and is precipitated therefrom by passage of carbon dioxide. In common with other phenolic bases of the cinchona series, it forms neutral salts, which are intensely yellow in aqueous solution, the colour being discharged by the addition of acids. It is non-fluorescent, and does not respond to the thalleioquin test. A series of alkyl ethers has been prepared in Europe, America, and in Japan, which promise to be of similar interest to the corresponding ethers of hydrocupreine (*see* Buttle, Henry, Solomon, Trevan and Gibbs, Biochem. J. 1938 **32**, 47). The methyl ether is *β-iso*quinine. apo*Quinine hydrochloride* crystallises from water or alcohol, m.p. 272·5°, $[\alpha]_D$ −163·8° in water. The *acid sulphate*, when anhydrous, has $[\alpha]_D$ −223° in water; the *sesquioxalate* melts at 225°, and the *dihydrobromide*, which crystallises from alcohol, m.p. 255°, $[\alpha]_D$ −180·9° in water, tends to lose HBr by dissociation.

isoapo*Quinine*, *a-iso*cupreine, is the geometrical isomeride of *apo*quinine, which it greatly resembles, and on methylation yields *a-iso*quinine. It is formed together with *apo*quinine and hydroxyhydro*apo*quinine when quinine is demethylated with sulphuric acid (Henry, Solomon and Gibbs, J.C.S. 1935, 967). It occurs in the mother-liquors from the acid sulphate or dihydrobromide fractionations of impure *apo*quinine. The latter salt, however, although the more soluble of the two in alcohol, is the less soluble in water. The base crystallises from acetone containing a little alcohol with the equivalent of $3H_2O$, or preferably from methyl alcohol. It froths at 190° and finally decomposes at 275°. The substance, like *a-iso*quinine, is remarkable for its high optical rotation, the anhydrous base having $[\alpha]_D^{15}$ −261·7° (c= 0·775 in alcohol), or −364°in dilute acid. The *hydrochloride* has m.p. 271° and $[\alpha]_D$ −194·5° in water; the *dihydrobromide* has m.p. 136°–140°, being thereby readily distinguished from *apo*quinine dihydrobromide, which melts at 255°.

Quinotoxine (quinicine),

$$CH_3O—C_9H_5N—CO—CH_2—CH_2—C_5H_9N—CH{=}CH_2,$$

is said to occur in cinchona bark, but is best prepared from quinine or quinidine, either by heating their acid sulphates (Pasteur, Compt. rend. 1853, **37**, 111; Hesse, Annalen, 1875, **178**, 245), or by boiling the bases with dilute acetic acid (von Miller, Rohde and Fussenegger, Ber. 1900, **33**, 3228). It has also been obtained by heating quinine with glycerol at 210° (Hesse, Annalen, 1873, **166**, 277). Quinotoxine is a yellowish amorphous mass, which becomes an oil at about 50° to 60°. It has $[\alpha]_D^{15}$ $+44{\cdot}1°$ ($c=2$ in chloroform) (Hesse), or $+38{\cdot}7°$ (Howard and Chick, J.S.C.I. 1909, **28**, 55). It is almost insoluble in water, but readily soluble in alcohol, ether or chloroform. It is a strong base which absorbs carbon dioxide from the air, and dissolves, when freshly precipitated, in ammonium salt solutions, expelling ammonia. It dissolves in mineral acids with a yellow colour, but does not fluoresce. With chlorine water and ammonia it produces the characteristic green coloration (thalleioquin). *Quinotoxine hydrochloride* ($B{\cdot}HCl$) is recommended for the isolation of the toxine; it has m.p. 180°–182°, $[\alpha]_D$ $+15°$ (average) in water (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1919, **41**, 832). The *neutral sulphate*, $B_2{\cdot}H_2SO_4,3H_2O$, crystallises from alcohol in prisms, and dissolves readily in water. The *oxalate*, $B_2{\cdot}C_2H_2O_4,9H_2O$, often used for the isolation of the toxine, crystallises from chloroform or alcohol, and is very sparingly soluble in water; the anhydrous salt has m.p. 166°–167°, $[\alpha]_D^{20}$ $+24°$ ($c=2$ in 1 vol. alcohol and 2 vols. chloroform) (Dirscherl and Thron, Annalen, 1935, **521**, 64). Other crystalline salts are the hydriodide, thiocyanate, tartrate, and platinichloride. Quinotoxine is a ketonic secondary-tertiary base. Its p-*bromophenylhydrazone* melts at 141°, and its **N**-methyl-derivative, identical with the "methylquinine" of Claus and Mallmann (Ber. 1881, **14**, 79) and the "methylquinidine" of Claus (Annalen, 1892, **269**, 234), can be obtained either by direct methylation or by boiling quinine or quinidine methiodide with aqueous alkali (phenylhydrazone, m.p. 135°–136°). Quinotoxine forms an *iso*nitroso- derivative with amyl nitrite, and a **N**-nitroso- derivative (nitrosamine) with nitrous acid.

epi*Quinine*, $C_{20}H_{24}O_2N_2$, is epimeric with quinine about the carbinol ($CH{\cdot}OH$) group. It occurs naturally, and can be isolated from "quinoidine" (Dirscherl and Thron, Annalen, 1935, **521**, 48), but was first obtained by epimerisation of quinine or quinidine by boiling with amyl alcoholic potassium hydroxide when there is formed a mixture in dynamic equilibrium of quinine, quinidine, *epi*quinine and *epi*-quinidine. The quinine and quinidine being removed as neutral and acid tartrate respectively, the two *epi*-bases are isolated together as dihydrochlorides; the *epi*quinine is then separated as the sparingly soluble dibenzoyltartrate, which cannot be recrystallised, and can only be purified by recovering the base and converting back to dibenzoyltartrate. The pure base is a colourless, viscous oil, $[\alpha]_D^{22}$ $+43{\cdot}3°$ ($c=0{\cdot}9494$ in alcohol). It is readily soluble in most organic solvents, and is more strongly fluorescent in dilute sulphuric acid than the parent alkaloids. Its *dihydrochloride* crystallises from acetone, m.p. 196°, $[\alpha]_D$ $+33{\cdot}3°$ in alcohol, and its dibenzoyltartrate, also from acetone, has m.p. 159° (Rabe *et al.*, Annalen, 1932, **492**, 252.)

Quininone,

$$CH_3O{-}C_9H_5N{-}CO{-}C_7H_{11}N{-}CH{=}CH_2,$$

is obtained in low yield by the gentle oxidation of quinine or quinidine with chromic acid (Rabe and Kuliga, Annalen, 1909, **364**, 346, 349). It is best prepared indirectly from quinotoxine by **N**-bromination with sodium hypobromite, followed by treatment of the **N**-bromotoxine (m.p. 123°), with sodium ethoxide (Rabe, Z. angew. Chem. 1913, i, 543; Rabe and Kindler Ber. 1918, **51**, 466). It separates in almost colourless crystals from ether, melts at 101° (108°), and shows mutarotation, the final value at 20° being $+75{\cdot}5°$ ($c=2$ in alcohol) (Rabe, Kuliga and Marschall, Annalen, 1910, **373**, 116, 117). It is readily soluble in most organic solvents, but not in water. It dissolves slightly in aqueous alkalis with a yellow colour (enolisation). The *hydrochloride*, $B{\cdot}HCl$, forms a very hygroscopic pale yellow, crystalline powder, m.p. 210°–212°, $[\alpha]_D$ (final value) $+58{\cdot}5°$ in alcohol. Quininone forms a glassy, *oxime* and on reduction in a suitable manner gives rise to quinine and quinidine (Rabe and Kindler, *l.c.*). With amyl nitrite and sodium ethoxide it is split into quininic acid and oximinovinylquinuclidine.

Quinine Chloride,

$$CH_3O{-}C_9H_5N{\cdot}CHCl{-}C_7H_{11}N{-}CH{=}CH_2,$$

is prepared from anhydrous quinine hydrochloride, chloroform and phosphorus pentachloride (Comstock and Koenigs, Ber. 1884, **17**, 1988; Rabe, Annalen, 1910, **373**, 103; Giemsa and Halberkann, Ber. 1921, **54**, [B], 1192). It crystallises from benzene, or benzene and ether, in magnificent colourless crystals, m.p. 151°–152°, $[\alpha]_D$ $+60{\cdot}3°$ to $+62{\cdot}6°$ in alcohol. *Quinine bromide* (C. F. Böhringer & Soehne, G.m.b.H., Rabe, Cohausz and Scheel, G.P. 592541/1932) has m.p. 154°.

Desoxyquinine,

$$CH_3O{-}C_9H_5N{-}CH_2{-}C_7H_{11}N{-}CH{=}CH_2,$$

is prepared by reducing a dilute sulphuric acid solution of quinine chloride with iron filings at room temperature (Koenigs, Ber. 1896, **29**, 372; Rabe, Annalen, 1910, **373**, 107; Giemsa and Halberkann, Ber. 1921, **54**, 1197). It crystallises from moist ether or from aqueous alcohol or acetone in colourless, efflorescent needles, $B{\cdot}2H_2O$, m.p. about 50°. The anhydrous base, which is not readily obtained crystalline, has m.p. 94° and $[\alpha]_D$ about $+99°$ in alcohol. It is fluorescent in dilute sulphuric acid and shows the thalleioquin reaction.

Quinene,

$$CH_3O{-}C_9H_5N{-}CH{=}C{=}C_6H_{10}N{-}CH{=}CH_2,$$

is prepared by boiling quinine or quinidine chloride with alcoholic potash (Comstock and Koenigs, Ber. 1884, **17**, 1989; 1885, **18**, 1223; Giemsa and Halberkann, *ibid.* 1921, **54**, 1192). It crystallises from ether, ligroin, or aqueous acetone with $2H_2O$, m.p. rather indefinite between 67° and 90°. The anhydrous base has $[\alpha]_D$ $+52{\cdot}5°$ in alcohol. The *dihydrochloride*, $B{\cdot}2HCl,H_2O$ (Heidelberger and Jacobs, J. Amer. Chem. Soc. 1920, **42**, 1501), crystallises from a mixture of alcohol and ether in lemon-yellow needles ; the anhydrous salt has m.p. 180°–185°, and $[\alpha]_D$ +18·4° in water.

apo*Quinene*, 4-(6-hydroxy-3:4-diethylphenyl)-6-hydroxy-quinoline,

$$HO{-}C_9H_5N{-}C_6H_2(OH)(C_2H_5)_2$$

(Kenner and Statham, J.C.S. 1935, 299), is obtained by heating quinene with hydrobromic acid (sp.gr. 1·49) at 180° (Comstock and Koenigs, Ber. 1885, **18**, 1226 ; Koenigs, J. pr. Chem. 1900, **61**, 41). *apo*Quinene, which should not be confused with *apo*quinine, crystallises from aqueous alcohol, m.p. 246°–248°.

Quininal,

$$CH_3O{-}C_9H_5N{-}CH(OH){-}C_7H_{11}N{-}CH{=}O,$$

and its acyl (acetyl and benzoyl) derivatives,

$$CH_3O{-}C_9H_5N{-}CH(O{-}CO{-}R){-}C_7H_{11}N{-}CH{=}O,$$

are obtained from quinine and from its acyl derivatives by the action of ozone in cold chloroform solution. The resulting ozonides furnish on hydrolysis formaldehyde, hydrogen peroxide and the aldehydic substances in question. The latter are amorphous. Quininal has $[\alpha]_D$ −30° in chloroform; the acetyl- derivative has $[\alpha]_D$ −63·5°, and the benzoyl- derivative +79·4° (Seekles, Rec. trav. chim. 1923, **42**, 69).

Quitenine,

$$CH_3O{-}C_9H_5N{-}CH(OH){-}C_7H_{11}N{-}CO_2H$$

is obtained by oxidising a cooled solution of quinine in dilute sulphuric acid with potassium permanganate. It was first prepared by Kerner in 1869, and has been studied by Skraup (Ber. 1879, **12**, 1104 ; Annalen, 1879, **199**, 348 ; Monatsh. 1889, **10**, 40). It crystallises from dilute alcohol in prisms with $4H_2O$, m.p. 286° (*decomp.*), $[\alpha]_D$ −142·7° ($c=0{\cdot}1$ in alcohol of sp.gr. 0·958). The anhydrous substance has $[\alpha]_D$ −298° ($c=5$ in N-H_2SO_4) (Goodson, Henry and Macfie, Biochem. J. 1930, **24**, 881). It is insoluble in ether or water, and sparingly soluble in alcohol, aqueous alcohol, or ammonia ; it is readily soluble in acids or fixed alkalis, but from the latter is precipitated again by absorption of carbon dioxide from the air. Quitenine is fluorescent both in acid and in aqueous-alcoholic solution and responds to the thalleioquin test. On oxidation with chromic acid it gives rise to the same oxidation products (but no meroquinene) as result in the like oxidation of quinine. On demethylation with hydriodic acid it gives rise to the phenolic substance "quitenol" ("cupretenine") (von Bucher, Monatsh. 1893, **14**, 604), but suffers no other change. Quitenine gives an acetyl derivative, and forms salts both with mineral acids and with metals. The ethyl ester has m.p. 200°.

Quininic Acid, 6-methoxyquinoline-4-carboxylic acid, $CH_3O{-}C_9H_5N{-}CO_2H$, is the most readily isolated of the oxidation products of quinine, quinidine, their hydro- derivatives, and many of their derivatives and degradation products. It has been synthesised by Rabe and co-workers (*see* section 5*b*, p. 144*a*). The following properties are mainly from Skraup (Monatsh. 1881, **2**, 589), it crystallises from dilute hydrochloric acid in yellowish prisms, m.p. 280°, soluble in about 100 parts of boiling alcohol, almost insoluble in water, ether or benzene. It is readily soluble in mineral acids (with a yellow colour) and in alkalis. Alcoholic solutions of the acid show a blue or violet fluorescence, and it responds, but not in typical fashion, to the thalleioquin test. On demethylation it gives rise to xanthoquininic acid, and on oxidation with alkaline permanganate to 2:3:4-pyridinetricarboxylic acid. It forms a hydrochloride, and salts with barium, calcium, copper, and silver. Its *methyl ester* has m.p. 85°, and *ethyl ester* 69°.

6-*Methoxylepidine*, 6-methoxy-4-methylquinoline, $CH_3O{-}C_9H_5N{-}CH_3$, has been obtained by the hydrolysis of quinene (Koenigs, Ber. 1890, **23**, 2673 ; Kaufmann, *ibid.* 1913, **46**, 1829) and has been synthesised from anisidine by Pictet and Misner (*ibid.* 1912, **45**, 1802), and by Rabe and co-workers (*ibid.* 1931, **64**, 2492). It crystallises from boiling water or aqueous alcohol with $1H_2O$, has m.p. 50°–52°, b.p. 213° and forms a *picrate*, m.p. 223°, and a *sulphate* insoluble in alcohol. It shows a blue fluorescence in water. On demethylation with boiling hydrobromic acid it gives rise to *p*-hydroxylepidine.

epiQuinine.—*See under* Quinine.

Quinoidine is the name originally applied by Sertürner (1828), the discoverer of morphine, to the amorphous material extractable from the mother-liquors left after removing quinine from the total alkaloids of cinchona bark. The name quinoidine is still applied to residues from quinine manufacture, but as this now differs greatly from the method used by Sertürner, and as the other crystalline associates of quinine are now also recovered, the material which goes by this name to-day differs greatly from Sertürner's product. It contains a small proportion of quinotoxine, but consists largely, as has been shown recently, of *epi*quinine and *epi*quinidine, which may be accompanied by their dihydro-derivatives (Dirscherl and Thron, Annalen, 1935, **521**, 48 ; this paper also summarises the history of quinoidine). Two views have been held as to the origin of these amorphous bases : (*a*) that they actually occur in the bark, (*b*) that they originate by decomposition of the crystalline alkaloids during manufacture. Dirscherl and Thron are of opinion that the *epi*-bases at least pre-exist in the bark.

Quinotoxine.—*See under* Quinine. (p. 176*d*)

"Totaquina."—*See* p. 132.

T. A. H. and W. S.

CINCHONAMINE *v.* Cinchona Alkaloids) (this vol., p. 152*a*).

CINCHONICINE (*Cinchotoxine*) *v.* Cinchona Alkaloids (this vol., p.157*d*).

CINCHONIDINE *v.* Cinchona Alkaloids) (this vol., p. 152*b*).

CINCHONIGINE (*β*-iso*Cinchonine*) *v.* Cinchona Alkaloids (this vol., p. 156*c*).

CINCHONILINE (d-iso*Cinchonine*) *v.* Cinchona Alkaloids (this vol., p. 156*b*).

CINCHONINAL *v.* Cinchona Alkaloids (this vol., p. 158*d*).

CINCHONINE *v.* Cinchona Alkaloids (this vol., p. 154*b*).

CINCHONINONE *v.* Cinchona Alkaloids (this vol., p. 158*a*).

CINCHOPHEN PHENYLCINCHONINIC ACID 2-phenylquinoline-4-carboxylic acid.

CINCHOTENINE *v.* Cinchona Alkaloids (this vol., p. 159*a*).

CINCHOTICINE *v.* Cinchona Alkaloids (this vol., p. 163*c*).

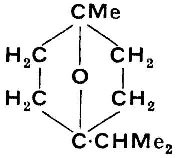
CINCHOTINE, DIHYDROCINCHONINE (*Hydrocinchonine*) *v.* Cinchona Alkaloids (this vol., p.).

CINCHOTINE *v.* Cinchona Alkaloids (this vol., p. 160*a*).

CINCHOTINETOXINE *v.* Cinchona Alkaloids (this vol., p. 162*d*).

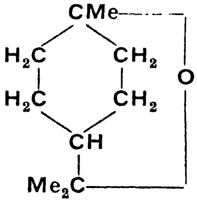
CINCHOTOXINE *v.* Cinchona Alkaloids (this vol., p. 163*c*).

1:4-CINEOLE.



1:4-*Cineole*, $C_{10}H_{18}O$, b.p. 172°, d^{18} 0·9010, n_D^{18} 1·4479, is present in small amount in the essential oil from the fruits of *Piper Cubeba*, grown in Mysore (Rao, Shintre and Simonsen, J.C.S.I. 1928, **47**, 92). It has been shown by Austerweil (Bull. Soc. chim. 1928, [iv], **45**, 862) to be present also in the low boiling fractions of the oil obtained in the manufacture of α-terpineol. 1:4-Cineole was first prepared by Wallach (Annalen, 1907, **356**, 204; 1912, **392**, 62) by the dehydration of *trans*-terpinene-terpin with oxalic acid. It can be obtained in a similar manner from *cis*-terpinene-terpin and from terpin hydrate (Dupont, Levy and Marot, Bull. Soc. chim. 1933, [iv], **53**, 393). With hydrogen chloride 1:4-cineole yields terpinene dihydrochloride. J. L. S.

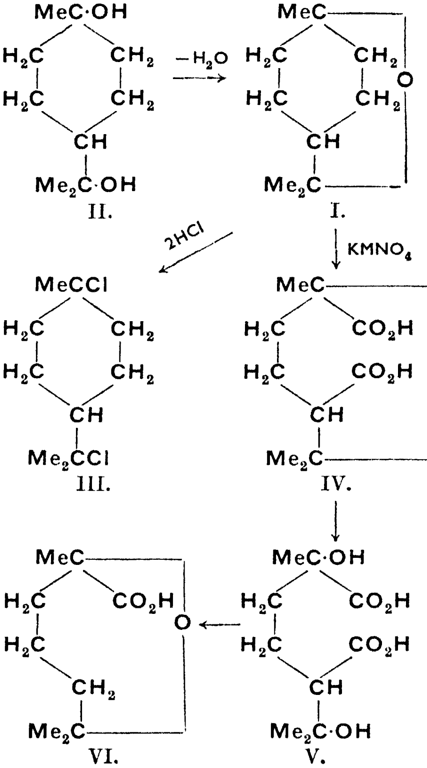
1:8-CINEOLE.



The oxide, 1:8-*cineole*, $C_{10}H_{18}O$, known also as eucalyptol and cajuputol, m.p. 3°, b.p. 174·4°/760 mm., d^{15} 0·930, n_D^{15} 1·45839, is one of the most widely distributed of essential oil constituents. It occurs, *inter alia*, in many eucalyptus oils, in *Oleum cina* (oil of wormseed) from *Artemesia maritima*, and in oil of cajuput from *Melaleuca minor*. It finds considerable use in pharmacy.

Cineole (I) can be obtained by the dehydration of *terpin* (II), whilst on treatment with hydrogen chloride it yields *dipentene dihydrochloride* (III), reactions which establish its structure. Cineole is extremely stable and distils unchanged over sodium. On oxidation with potassium permanganate it gives *cineolic acid* (IV), m.p. 204°–206° (Wallach, Annalen, 1888, **246**, 268; 1890, **258**, 319; 1892, **271**, 20), which when heated with water at 150° gives *cinogenic acid* (V), m.p. 104·5°–106°. This latter acid is converted into *a-cinenic acid* (VI), m.p. 83°–84°, when heated at 150° (Rupe, Ber. 1908, **41**, 3955; Helv. Chim. Acta, 1933, **16**, 505; 1934, **17**, 98).

Various methods have been suggested for the quantitative estimation of cineole. The two most satisfactory are the preparation of (i) its crystalline additive compound, $C_{10}H_{18}O,H_3PO_4$, which is formed when it is mixed with syrupy phosphoric acid or (ii) its compound with *o*-cresol, $C_{10}H_{18}O,C_7H_8O$, m.p. 55·8° (Cocking, Pharm. J. 1920, **105**, 81).



J. L. S.

CINNABAR. Native mercury sulphide, (HgS), and the only ore of this metal. Its crystals are rhombohedral, with perfect cleavages parallel to the faces of the hexagonal prism; they are of interest crystallographically in presenting the same type of trapezohedral symmetry as quartz, and, like this, they rotate the plane of plane-polarised light. They are bright-red in colour, often transparent, and have a brilliant adamantine to sub-metallic lustre; the scarlet streak is characteristic. Sp.gr. 8·1; hardness, 2–2½. The refractive indices are high: for the ordinary ray 2·81429, and for the extraordinary ray 3·14344 for red light (λ 672 $m\mu$); and n_E 3·27188 for sodium-light at 21°C. (H. Rose, Centr. Min. 1912, 527). The rotatory power is also very high (over 25 times that of quartz): for a thickness of 1 mm. the angle of rotation is 555° for sodium-light at 18·6°C. (H. Rose, N. Jahrb. Min. 1900, **29**, 94).

The massive ore, which may be compact or earthy in texture, is of the same colour ; but sometimes it is liver-brown or black, owing to the admixture of clay or organic matter, as in the varieties called respectively *hepatic cinnabar* and *coral-ore* (German, *Korallenerz*). Cinnabar is very sporadic in its distribution, and no mineral containing mercury has yet been found in the British Isles. It is mined at Almaden in Spain ; Monte Amiata in Tuscany; Idria in Carniola ; New Almaden in California; in the provinces of Kwei-chou and Hunan, in central China ; and in Mexico and Peru.

Metacinnbarite is the tetrahedral-cubic modification of **HgS**, of rare occurrence as small black crystals. Cinnabar and two other crystalline modifications of mercuric sulphide have been obtained artificially by E. T. Allen and J. L. Crenshaw (1912). Cinnabar is the stable form at all temperatures up to its sublimation point, about 580°.

L. J. S.

CINNAMALDEHYDE, cinnamic aldehyde, $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$, occurs in a number of essential oils, notably in cinnamon and cassia oils and forms an important article of commerce. It is extracted from oil of cinnamon by formation and subsequent decomposition of the crystalline sodium bisulphite compound (Peine, Ber. 1884, **17**, 2109) and from cassia oil by means of the double compound with barium sulphanilate (G.P. 124229).

Cinnamaldehyde is most conveniently prepared synthetically by allowing a mixture of 10 parts of benzaldehyde, 15 parts of acetaldehyde, 900 parts of water, and 10 parts of 10% sodium hydroxide solution to stand at 30° for 8–10 days with frequent shaking ; it is then isolated by ether extraction (Peine, Ber. 1884, **17**, 2117 ; *cf.* B.P. 10003). Two further synthetic methods of preparation from ω-chloroallylbenzene have been described (Bert and Dorier, Compt. rend. 1930, **191**, 332 ; Bert and Annequin, *ibid.* 1931, **192**, 1315) which are capable of extension to substituted cinnamaldehydes. It is best purified by means of the double compound with nitric acid (Dumas and Péligot, Ann. Chim. 1834, [ii], **57**, 322 ; Pfeiffer, Annalen, 1910, **376**, 298).

It is a colourless oil with a pleasant cinnamon-like odour ; m.p. −7·5° ; b.p. 252° (decomp.), 130°/20 mm. ; d_4^{20} 1·0497 ; n_D^{20} 1·6195. It should, theoretically, exist in two geometrically isomeric forms, and Bourguel (Bull. Soc. chim. 1929, [iv], **45**, 1067) has described the pure *cis*-compound, b.p. 111°–113°/16 mm. ; d^{20} 1·032; n_D^{20} 1·565, and its diethyl acetal. It is volatile in steam, practically insoluble in water and miscible in all proportions with alcohol. It may be characterised as its *phenylhydrazone*, m.p. 168°, *semicarbazone*, m.p. 215°, and 2:4-*dinitrophenylhydrazone*, m.p. 248°. It forms two *oximes*, *syn*-, m.p. 139°, and *anti*-, m.p. 76°, the orientation of which has been established by Brady and Thomas (J.C.S. 1922, **121**, 2098).

In the air it is oxidised mainly to cinnamic acid (*cf.* Pound and Pound, J. Physical Chem. 1934, **38**, 1045) whilst more drastic oxidation affords benzoic and acetic acids. Reduction with zinc-copper couple (Thiele, Ber. 1899, **32**, 1296) yields the dimeric product hydrocinnamoin, $(Ph{\cdot}CH{:}CH{\cdot}CH(OH))_2$, but it may be reduced to cinnamyl alcohol with iron and acetic acid (Pauly, Schmidt and Böhme, Ber. 1924, **57**, 1327). It is, however, best reduced by catalytic hydrogenation with platinum black ; this reaction is very sensitive to added impurity and by suitably adjusting the conditions either cinnamyl alcohol or γ-phenylpropyl alcohol may be produced (Tuley and Adams, J. Amer. Chem. Soc. 1925, **47**, 3061) ; electrolytic reduction also yields γ-phenylpropyl alcohol (Shima, Mem. Coll. Sci. Kyoto, 1929, [A], **12**, 69).

Cinnamaldehyde is estimated in essential oils volumetrically by means of hydroxylamine hydrochloride (Bennett and Donovan, Analyst, 1922, **47**, 146) or sodium bisulphite (Gildemeister and Hoffmann, "Die ätherischen Öle," 1928, Vol. 1, p. 743) and gravimetrically with semioxamazide (Hanuš, Z. Nahr.-Genussm. 1903, **6**, 817). *See* ALDEHYDES.

H. N. R.

CINNAMEIN *v.* BALSAMS, BALSAM OF PERU.

CINNAMIC ACID. β-Phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}CO_2H$. The separation of a solid acid from old specimens of oil of cinnamon was first observed in 1780 by Trommsdorf, but the acid was regarded as benzoic acid until this error was corrected by Bizio in 1826. Cinnamic acid was first closely investigated by Dumas and Peligot (Annalen, 1835, **14**, 56).

Cinnamic acid is very widely distributed in nature, the best known natural sources being liquid storax and tolu and Peru balsams. It is isolated from storax by boiling with sodium hydroxide, followed by precipitation with hydrochloric acid and recrystallisation (Beilstein and Kuhlberg, Annalen, 1872, **163**, 123 ; *cf.* von Miller, *ibid.* 1877, **188**, 196).

It is formed by heating benzaldehyde with acetyl chloride at 120°–130° (Bertagnini, Annalen, 1856, **100**, 126). This process was greatly modified and improved by Perkin (J.C.S. 1877, **31**, 388) who heated a mixture of benzaldehyde, acetic anhydride and anhydrous sodium acetate ; this reaction, which is known as the Perkin reaction, is that generally employed in the laboratory. An improved procedure is described by Meyer and Beer (Monatsh. 1913, **34**, 651) and Bacharach and Brogan (J. Amer. Chem. Soc. 1928, **50**, 3333) have shown that the addition of pyridine greatly increases the yield. The cinnamic acid used in the early processes for the manufacture of synthetic indigo was prepared by this method, but Caro (G.P. 17467, 18232) showed that it could be prepared more cheaply by heating benzal chloride with anhydrous sodium acetate: 1 part of benzal chloride and 2 to 3 parts of powdered fused sodium acetate are heated at 180°–200° for 10 to 20 hours in an autoclave with mechanical stirring. The melt is mixed with water, made alkaline with caustic soda and steam-distilled ; the residual solution is filtered hot, acidified, and cooled. The precipitated cinnamic acid is filtered off and recrystallised from water or alcohol.

Another process of technical importance consists in oxidising benzylideneacetone with sodium hypochlorite or hypobromite (G.P. 21162 ; Ullmann, " Enzyklopädie der technischen Chemie," 1921, Vol. IX, p. 613 ; Schorigin, Issaguliantz, and Gusseva, J. Gen. Chem. Russ. 1931, **1**, 506).

It may also be obtained by condensation of benzaldehyde with malonic acid in the presence of ammonia or certain amines (Knoevenagel, Ber. 1898, **31**, 2602 ; G.P. 97735, 164296).

Cinnamic acid forms colourless, monoclinic, prismatic crystals, m.p. 133°, b.p. 300°. It is soluble in 3,500 parts of water at 17°, in 4·2 parts of ethyl alcohol at 20°, in 17 parts of chloroform at 15°, and is volatile in steam. It may be characterised as its *amide*, m.p. 148°, p-*bromophenacyl ester*, m.p. 145°, and p-*phenylphenacyl ester*, m.p. 182°. It forms crystalline salts closely resembling those of benzoic acid. Oxidising agents convert it first into benzaldehyde (distinction from benzoic acid) and afterwards into benzoic acid, the final products when potassium permanganate is used being phenylglyceric acid, benzaldehyde, and benzoic and oxalic acids (Fittig and Ruer, Annalen, 1892, **268**, 27). On fusion with caustic potash it yields a mixture of benzoate and acetate. It may be determined by direct titration, by absorption of bromine or by oxidation to benzoic acid (Nicholls, Analyst, 1928, **53**, 19).

It is now generally accepted that cinnamic acid exists in four forms (Stobbe, Ber. 1911, **44**, 2739): (1) ordinary cinnamic acid, m.p. 133°; (2) *allo*cinnamic acid, m.p. 68° ; (3) and (4) two *iso*cinnamic acids, m.p. 42° and 58°. Of these (1) is the *trans*- acid and (2), (3), and (4) trimorphs of the *cis*- acid, (2) being stable and (3) and (4) labile (Biilmann, Ber. 1910, **43**, 568). Meyer and Pukall (Z. physikal. Chem. 1929, **145**, 360), however, conclude from work on the bromine addition of the various forms that the three last are truly isomeric and not merely polymorphic. This view is not accepted by Robinson and James (J.C.S. 1933, 1453). From physical data Eisenlohr and Hass (Z. physikal. Chem. 1935, **173**, 249) conclude that the three *cis*- acids are some special kind of rotational isomers ; this view is contested by Meyer (*ibid*. 1935, **174**, 77).

In the polymerisation of cinnamic acid the following equilibria are set up (Stobbe *et al*., Ber. 1919, **52**, [B], 666 ; 1925, **58**, [B], 1548, 2415, 2859; 1926, **59**, [B], 2254):

$$\begin{tikzcd}
\alpha\text{-truxillic acid} \arrow[r, shift right, "\text{short waves}"'] & \textit{trans}\text{-cinnamic acid.} \arrow[l, shift right, "\text{long waves}"'] \arrow[d, shift right] \\
\beta\text{-truxinic acid} \arrow[r, shift right, "\text{short waves}"'] & \textit{cis}\text{-cinnamic acid.} \arrow[l, shift right, "\text{long waves}"'] \arrow[u, shift right]
\end{tikzcd}$$

Cinnamic acid may be reduced to β-phenylpropionic acid (*hydrocinnamic acid*) by a wide range of methods, among which may be mentioned catalytic hydrogenation (Paal and Gerum, Ber. 1908, **41**, 2277; Vavon, Compt. rend. 1909, **149**, 999 ; Böeseken, Rec. trav. chim. 1916, **35**, 270, 277, 285), reduction with sodium amalgam (Alexejew and Erlenmeyer, Annalen, 1866, **137**, 327) and with formic acid in the presence of palladium black (G.P. 267306). It forms a *dibromide*, m.p. 201°, with bromine in a variety of solvents (Sudborough and Thompson, J.C.S. 1903, **83**, 669 ; Fittig and Binder, Annalen, 1879, **195**, 140 ; Michael, J. pr. Chem. 1895, [ii], **52**, 292 ; Ber. 1901, **34**, 3664), while addition of hydrogen bromide gives *β-bromo-β-phenylpropionic acid* (Fittig and Binder, *l.c.*) other halogen hydrides behaving similarly.

Cinnamic acid condenses with hydrocarbons, *e.g.* with benzene and sulphuric acid it forms *phenylhydrindone* (Liebermann and Hartmann, Ber. 1892, **25**, 2124), and with phenols, *e.g.* with phenol, it yields *hydroxyphenylcoumarin* (*idem.*, *ibid.* 957).

Esters.—Stoermer and Sandow (Ber. 1920, **53**, [B], 1283) have formulated the general rule that the esters of *cis*- forms of substituted cinnamic acids have lower boiling-points than those derived from the corresponding *trans*- acids.

Methyl cinnamate.—Crystalline solid, m.p. 36°, b.p. 263°, 127°/10 mm.

Ethyl cinnamate is obtained directly by the condensation of benzaldehyde and ethyl acetate by means of sodium (Claisen, Ber. 1890, **23**, 977 ; Posner, J. pr. Chem. 1910, [ii], **82**, 435; B.P. 4969, 1890 ; G.P. 53671 ; Marvel and King, Organic Syntheses, 1929, **9**, 38). It is a colourless liquid, b.p. 271°, 144°/15 mm.

Substituted Cinnamic Acids.—o-*Nitrocinnamic acid* was formerly of importance for the manufacture of synthetic indigo. Nitration of the free acid (Müller, Annalen, 1882, **212**, 126) or of the ethyl ester (Friedländer, " Fortschritte der Teerfarbenfabrikation," 1888, **1**, 125) yields a mixture of the *o*- and *p*-nitrocompounds which are separated by taking advantage of the insolubility of ethyl *p*-nitrocinnamate in alcohol (Drewsen, Annalen, 1882, **212**, 150). *o*-Nitrocinnamic acid exists in two forms, *trans*-, m.p. 240°, and *cis*-, m.p. 143°, the former being produced by nitration; similarly it is *trans*-*p*-nitrocinnamic acid, m.p. 286°, which is formed by nitration, the *cis*- acid melting at 143° (*see* CARBOXYLIC ACIDS).

H. N. R.

CINNAMIC ALCOHOL, Cinnamyl alcohol

$C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$

(AND ESTERS). Cinnamic alcohol is a synthetic perfume with a soft hyacinth odour, and is used as such and also in the form of its esters in modern perfumery. Pure cinnamic alcohol melts at about 33°, but commercial samples often contain traces of impurities which keep it in a liquid condition. B.p. 257°–258° ; d^{36}_{4} 1·0302 ref. index, about 1·580. Cinnamyl acetate, butyrate, and cinnamate which are used as synthetic perfumes have balsamic odours, and are of value in imparting special nondescript odours to compound perfumes.

E. J. P.

CINNAMON and CASSIA. In the United States the terms cinnamon and cassia are used almost indiscriminately, although it is there recognised that, strictly speaking, they belong to two entirely separate trees. In Great Britain they are treated as separate entities even in commerce, the price of cinnamon being two or three times that of cassia. For convenience the two spices are treated together.

Cinnamon is the dried inner bark of *Cinnamomum zeylanicum* Nees (Fam. Lauraceæ), a tree which grows to a height of 20 to 30 feet and which is native to Ceylon. In practice, the young trees are pruned to produce a straight stem, which is then cut back and shoots are allowed to grow out from the stump. The branches are cut when they are between 1 and 2 cm. in diameter ; the bark is slit longitudinally with two or more cuts and horizontally every 30 cm., and removed by copper or brass knives to prevent discoloration of the tannin. The strips are made into mats and allowed to ferment, after which the outer epidermis and the cortex are removed, leaving only the intermediate layer of the bark. The narrower pieces are then placed inside larger ones and the whole curled together to make, when dried, the quills of commerce. The outer surface is dull and pale yellowish-brown in colour, the inner surface being light brown and marked with faint longitudinal striations. On the outer surface, the longitudinal striations are more definite, and there are frequent scars and sometimes holes due to leaves. The bark is very brittle and breaks with a splintery fracture. The odour is fragrant and the taste sweetish and warmly aromatic.

Cassia is the dried bark of *Cinnamomum Cassia* Blume (Fam. Lauraceæ), and less care is taken with its cultivation than with genuine cinnamon. The outer bark is partly removed by shaving, but much of this and the whole of the innermost bark are left in the quills, making them thicker and stronger than those of cinnamon. The colour is dark earthy-brown with occasional patches of a greenish colour showing where the outer surface of the bark still persists. The fracture is short and granular but fibrous on the inside. The odour and taste are similar to but coarser than those of cinnamon, and the taste is also more stringent and slightly mucilaginous.

Microscopic Examination of the two barks shows many similarities. In true cinnamon the sclerenchymatous cells form an uninterrupted ring, whereas in cassia there is an uninterrupted ring due to the outer bark, but in the inner bark, corresponding to the portion used for cinnamon, the sclerenchymatous cells do not form a continuous ring. These cork cells of the outer bark of cassia are much smaller than those of the inner portion. The sclerenchymatous cells of the phelloderm, or inner bark, are slightly elongated tangentially, but thickened on the inner walls, this thickening being more conspicuous with cassia than with cinnamon. The number of starch grains is about the same in both barks, although cassia starch grains are larger than those of cinnamon. The bast fibres of both barks are large and thick-walled, being larger in cassia than in cinnamon. Most of the secretion cells of both barks are empty, though some are filled with yellowish volatile oil or resin. Both barks contain minute prismatic crystals of calcium oxalate.

Both cinnamon and cassia are largely employed as flavouring materials and also for their carminative properties. Cassia buds are used as well as the barks for the distillation of the essential oils, and the leaves of both trees are distilled for their oils, but these latter differ considerably from the bark oils.

Chemical Composition.—Liverseege (" Adulteration and Analysis of Foods and Drugs," 1932, p. 427) Winton, Ogden and Mitchell (22nd Ann. Report Conn. Exp. Sta. 1898, 204), C. Arragon (Ann. Falsif. 1915, **8**, 345), and Richardson (U.S. Dept. of Agric. Div. of Chem., Bull. 13, 221) all record figures for the composition of cinnamon and cassia, and since these vary considerably they are quoted separately in the following table :

	CINNAMON.				CASSIA.		
Author . .	Liverseege.	Winton, etc.	Arragon.	Richardson.	Winton, etc.	Arragon.	Richardson.
No. of samples	approx. 15	6	2	2	20	2	4
	%	%	%	%	%	%	%
Moisture .	8·9–10·5	7·79–10·48	8·2–11·4	5·4–7·3	6·5–11·9	10·5–11·0	9·3–17·4
Ash . . .	3·9–6·0	4·2–6·0	3·5–4·3	3·4–4·5	3·0–6·2	1·9–2·9	2·5–8·2
Sand . .	0·04–0·6	0·02–0·13			0·02–2·42		
Cold alcohol extract .	7·6–13·0	10·0–13·6			4·6–16·7		
Volatile oil .	0·5–1·1	0·7–1·6	2·5–2·8	0·8–1·1	0·9–5·1	2·6	0·5–3·5
Fixed oil .	1·1–3·3	1·35–1·68	0·5–1·2	1·6–1·7	1·3–4·1	1·3–1·5	0·7–2·4
Starch and reducing substances		16·6–22·0	19·3–22·6		16·9–32·0	31·7–33·9	
Crude fibre		34·4–38·5	31·4–34·7	25·6–33·1	17·0–28·8	25·2–26·0	14·3–26·3
Protein . .		3·2–4·1	3·4–4·3	3·0–3·8	3·3–5·4	3·1–3·4	2·6–4·5

The principal constituent is the essential oil, and this is probably determined most satisfactorily by the method of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435). The powdered bark is mixed with brine, distilled, and the vapours passed through the top of a condenser into a graduated tube, into which a small quantity of turpentine has been previously distilled to make the mixture lighter than water, the condensed water itself being returned to the distillation flask. An air inlet and outlet is provided by a side tube between the bottom of the condenser and the graduated tube. Cinnamon bark contains from 0·5 to 1·0%, and cassia bark from 0·5 to 2·0% of volatile oil, as distilled in commerce.

Standards.—The "British Pharmacopœia" requires that cinnamon shall contain not more than 7% of ash, and acid insoluble ash not more than 2%.

Adulteration.—Cassia bark is often supplied instead of the true cinnamon, whilst other species of cinnamon and cinnamon from the true *Cinnamomum zeylanicum*, but grown wild in Seychelles, are passed off for either bark.

T. McL.

CINNAMON BARK, ESSENTIAL OIL OF. The oil distilled from the bark of *Cinnamomum zeylanicum* Nees (Fam. Lauraceæ), a small tree indigenous to and cultivated in Ceylon. An inferior oil is produced in the Seychelles, where the tree is cultivated. The oil is distilled mainly from the chips and refuse bark after the collection of the cinnamon quills for the spice trade. Formerly a mixture of bark and leaves was used for distillation, but the oil thus obtained contains a considerable amount of eugenol and is not suitable for use in medicine. The finest oil is produced in limited quantities and is an expensive product.

Constituents.—The main constituent is cinnamaldehyde. Pinene, phellandrene, and cymene are present, and traces of methyl-*n*-amyl ketone, benzaldehyde, nonaldehyde, furfural, linalool, and caryophyllene.

Characters.—A pale yellow oil becoming darker on keeping, sp.gr. 1·000 to 1·040, opt. rot. 0° to −1° at 20°, n_D^{20} 1·565 to 1·591. Soluble in 4 volumes of 70% alcohol. Cinnamaldehyde content, 50 to 65% ("British Pharmacopœia" standard), determined by the hydroxylamine method. English distilled oils usually comply with these requirements, but less fragrant oils containing up to 75% are found in commerce at lower prices. Inferior oils containing admixtures of artificial cinnamaldehyde and distilled cassia oil are offered on the English market. It should be noted that the cinnamon oil official in the "United States Pharmacopœia" is redistilled cassia oil (*q.v.*). The Seychelles oil of cinnamon bark contains only 20 to 35% of cinnamaldehyde and is not soluble in 70% alcohol.

C. T. B.

CINNAMON LEAF, ESSENTIAL OIL OF. The oil distilled from the leaves of *Cinnamomum zeylanicum* Nees (Fam. Lauraceæ) differs entirely from the oil obtained from the bark of the same tree (*v.* CINNAMON BARK, ESSENTIAL OIL OF). It is produced in large quantities in Ceylon and also in the Seychelles. It is used in soap perfumery and constitutes a valuable source of eugenol.

Constituents.—Eugenol, *l*-α-pinene, *l*-phellandrene, dipentene, benzaldehyde, linalol, terpineol, borneol, geraniol, safrole, α- and β-caryophyllene, benzyl benzoate, cinnamaldehyde, cinnamyl alcohol, and traces of other alcohols are present.

Characters.—Sp.gr. 1·040 to 1·060, opt. rot. −1° to -3° at 20°, n_D^{20} 1·530–1·545, phenolic constituents 70–90%. Soluble in 3 volumes of 70% alcohol. The phenolic constituents are determined by adsorption in the cold with aqueous 5% solution of potassium hydroxide.

C. T. B.

CINNAMON-STONE or HESSONITE. A gem-variety of garnet of a warm reddish-brown colour (hence the name) and transparent. It is essentially an orthosilicate of calcium and aluminium, $Ca_3Al_2Si_3O_{12}$, containing, however, isomorphous replacements of iron, manganese and magnesium. Brilliant crystals are found in veins in serpentine at Ala in Piedmont, but material of the best gem-quality is found as pebbles in the gem-gravels of Ceylon.

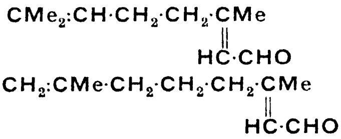
L. J. S.

CINOBUFAGIN *v.* CARDIAC GLYCOSIDES, TOAD POISONS.

CITOBARYUM. Prepared barium sulphate for use as a barium meal (*Merck, Darmstadt, Napp, London*), B.P.C. 1934.

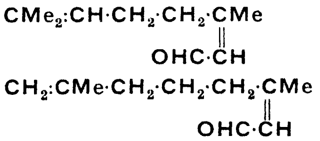
CITRALS, THE.

Citral a. (*Geranial.*)



$$\begin{array}{l} CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad HC{\cdot}CHO \\ CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad HC{\cdot}CHO \end{array}$$

Citral b. (*Neral.*)



$$\begin{array}{l} CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad OHC{\cdot}CH \\ CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe \\ \qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad OHC{\cdot}CH \end{array}$$

Citral is the most important natural acyclic aldehyde of the terpene series. It occurs very widely distributed in nature and it forms the main constituent of lemon grass oil (from *Cymbopogon flexuosus Stapf*). It finds wide technical application both directly in the perfume industry and also indirectly for synthetic purposes. The natural aldehyde is a mixture of the four aldehydes represented by the formulæ given at the head of the section.

Citral a, $C_{10}H_{16}O$, b.p. 118–119°/20 mm., d^{20} 0·8898, n_D^{20} 1·4891, is most readily obtained from lemon grass oil, of which it forms approximately 90% of the aldehyde content, by the preparation of its crystalline sodium bisulphite compound (Tiemann, Ber. 1899, **32**, 117; Hibbert and Cannon, J. Amer. Chem. Soc. 1924, **46**, 119). It yields a *semicarbazone*, m.p. 164°. It is obtained also, almost free from citral *b*, by the oxidation of geraniol (Zeitschel, Ber. 1906, **39**, 1787).

Citral b, b.p. 117–118°/120 mm., d^{20} 0·8888, n_D^{20} 1·4981, *semicarbazone*, m.p. 171°, is separated from citral *a* by taking advantage of the more ready reaction of the latter with cyanoacetic acid (Tiemann, Ber. 1899, **32**, 120). It can be obtained also by the oxidation of nerol. Both aldehydes are, when freshly distilled, colourless liquids with a characteristic odour ; they oxidise rapidly on exposure to the air becoming yellow in colour.

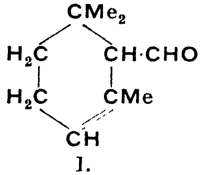
The structures assigned to the two aldehydes follow from their preparation by the oxidation of the primary alcohols geraniol and nerol. On oxidation with silver oxide citral yields *geranic acid* (Semmler, Ber. 1890, **23**, 2965, 3556), which is obtained also by the conversion of citral oxime into geranionitrile followed by hydrolysis (Tiemann and Semmler, Ber. 1893, **26**, 2717). On oxidation with potassium permanganate followed by chromic acid citral yields a mixture of acetone, levulinic and oxalic acids (Tiemann and Semmler, Ber. 1895, **28**, 2132). In agreement with these results Harries (Ber. 1903, **36**, 1933 ; 1907, **40**, 2823 ; Annalen, 1905, **343**, 351 ; *cf.* Grignard, Doeuvre and Escourrou, Bull. Soc. chim. 1924, **35**, 932) has found that the citral semicarbazones, yield on oxidation with ozone, formaldehyde, acetone, lævulinaldehyde and probably glyoxal. Confirmation of the structure assigned to the aldehydes is provided also by their degradation by alkali to *methylheptenone*.

Citral has been prepared synthetically by the distillation of a mixture of calcium geranate and calcium formate (Tiemann, Ber. 1898, **31**, 828).

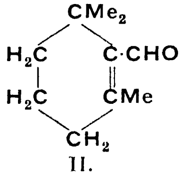
Citral can be characterised by the preparation of a number of derivatives and since in essential oils citral *a* predominates derivatives of this aldehyde are as a rule obtained. In addition to the semicarbazones referred to above, suitable derivatives are a-*citrylidene cyanoacetic acid*, m.p. 122° ; b-*citrylidene cyanoacetic acid*, m.p. 94°, and a-*citryl-β-naphthocinchonic acid*, m.p. 198–200°.

On catalytic hydrogenation in the presence of colloidal palladium citral yields a mixture of citronellol and citronellal (Skita, Ber. 1909, **42**, 1634) ; and with platinum black a mixture of 2:6-dimethyloctane and 2:6-dimethyloctanol is formed (Vavon, Ann. Chim. 1914, [ix], **1**, 169), whilst with platinic oxide Adams and Garvey (J. Amer. Chem. Soc. 1926, **48**, 477) obtained geraniol, citronellol, and 2:6-dimethyloctanol.

Citral shows a marked tendency to undergo cyclisation passing into *p*-cymene in the presence of mineral acids. If, however, either of the isomeric citrylidene cyanoacetic acids is heated with dilute sulphuric acid a mixture of α- and β-cyclo*citrylidene cyanoacetic acids* is obtained, which yields on hydrolysis with alkali α- and β-cyclo*citrals* (I) and (II), the latter being formed in the larger quantity (Steubel, G.P. 108335 ; Tiemann, Ber. 1900, **33**, 3709). Haarmann and Reimer (G.P. 123747) have shown that the treatment of the condensation product of citral and aniline with concentrated sulphuric acid gives a mixture of the *cyclo*-citrals. Merling (Ber. 1908, **41**, 2064) has also described methods for the preparation of these cyclic aldehydes.



I.



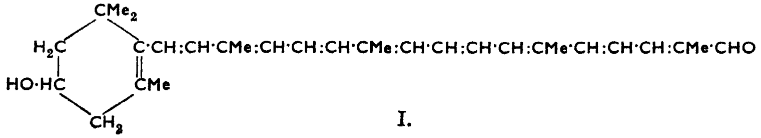
II.

For the separation of α-*cyclo*citral, b.p. 90–95°/20 mm., d^{15} 0·925, *semicarbazone*, m.p. 206°, advantage is taken of the fact that when a mixture of the two aldehydes is reduced with sodium amalgam β-*cyclo*citral is converted into high boiling products whilst α-*cyclo*citral is not attacked. It yields on oxidation α-cyclo-*geranic acid*, m.p. 103·5°. It condenses with acetone to yield α-ionone. β-*Cyclo*citral, b.p. 112–114°/29 mm., $d^{15·25}$ 0·9586, $n_D^{13·3}$ 1·4970, *semicarbazone*, m.p. 166–167°, is obtained free from α-*cyclo*citral by distilling a mixture of the semicarbazones of the two aldehydes in steam in the presence of phthalic acid when only β-*cyclo*-citral semicarbazone is hydrolysed. On oxidation it gives a mixture of β-*cyclo*geranic and geronic acids. It condenses with acetone to give β-ionone.

Citral *a* condenses with acetone to yield α-*pseudoionone*, b.p. 159–165°/20 mm., d^{20} 0·8954, n_D 1·5317, *semicarbazone*, m.p. 142°, whilst from citral *b* β-*pseudoionone*, b.p. 146–150°/15 mm., d^{15} 0·898, n_D 1·53446, *semicarbazone*, m.p. 143–144°, is obtained (Tiemann, Ber. 1898, **31**, 2318 ; 1899, **32**, 827 ; 1900, **33**, 882 ; Friedländer III, 889 ; G.P. 122466, 127661, 130457 ; Hibbert and Cannon, J. Amer. Chem. Soc. 1924, **46**, 119). Analogous compounds with other ketones have been prepared (G.P. 150771).

J. L. S.

CITRAURIN. This pigment, which separates in red needles from aqueous methyl alcohol, m.p. 144–145°, is one of several carotenoids which pigment the ripe orange (*Citrus aurantium*), others being kryptoxanthin, zeaxanthin, lutein, carotene, and violaxanthin (Zechmeister and Tuzson, Ber. 1936, **69**, [B], 1879). Citraurin, a polyene aldehyde, exhibits absorption maxima at 486 and 457 mμ in carbon disulphide ; the oxime, m.p. 181–182°, possesses absorption maxima at 504 and 473 mμ in carbon disulphide. The structure (I) was proposed for citraurin by Karrer and Solmssen (Helv. Chim. Acta, 1937, **20**, 682) ; this has been established by Zechmeister and Cholnoky (Annalen, 1937, **530**, 291) who effected the degradation of capsanthin to citraurin by heating in a sealed tube with aqueous-alcoholic potassium hydroxide.



I.

Citraurin is also obtained by the partial oxidation of zeaxanthin with potassium permanganate (Karrer, Solmssen and Gugelmann, Helv. Chim. Acta, 1937, **20**, 1020).

I. M. H., R. F. P., and F. S. S.

CITRIC ACID, $C_6H_8O_7$.

Occurrence.—This acid occurs in the free state in the juice of many acid fruits such as lemons, currants, cranberries, limes, etc. It is also found free or as salts in the seeds and juices of many flowers and plants. It is a constituent of wine, milk, cheese, and animal tissues and fluids.

Synthesis.—The acid can be prepared from *sym*-dichloroacetone by treatment with hydrocyanic acid and hydrochloric acid, whereby dichloroacetonic acid is formed. This is then neutralised with sodium carbonate and heated with potassium cyanide. The resulting solution of dicyanoacetonic acid is saturated with hydrogen chloride and heated on a water bath for 15 hours. The citric acid formed can be separated as calcium citrate by neutralising with milk of lime (Grimaux and Adam, Compt. rend. 1880, **90**, 1252). It has been prepared by the action of potassium cyanide and hydrochloric acid on ethyl acetonedicarboxylate (Dünschmann and von Pechmann, Annalen, 1891, **261**, 162). Ethyl citrate has been obtained in small quantities by heating together ethyl bromoacetate and ethyl oxalylacetate in the presence of zinc (Lawrence, Chem. Soc. Proc. 1897, **13**, 65).

Physical Properties.—Citric acid crystallises from cold aqueous solutions with 1 mol. of water. The crystals belong to the orthorhombic system (Groth, Chemische Krystallographie, 1910, **3**, 475), and have a sp.gr. of 1·553. They are stable in air of ordinary humidity but lose water rapidly in dry air (Marchand, J. pr. Chem. 1842, [i], **23**, 61). On warming slowly they soften at about 70°–75° with loss of water and finally melt completely between 135° and 152° (Buchner and Witter, Ber. 1892, **25**, 1160). If the crystals are rapidly heated they melt at about 100°, then solidify as they become anhydrous, and melt sharply at 153° (Meyer, Ber. 1903, **36**, 3599). The acid is obtained anhydrous by cooling its hot, concentrated solutions (Buchner and Witter, *l.c.*; Meyer, *l.c.*). The mean transition point at which the anhydrous and hydroated forms may separate from solution is 36·3°±0·15° (Bennett and Yuill, J.C.S. 1935, 130). The latter workers give a crystallographic description of the anhydrous form of citric acid which crystallises in the holohedral class of the monoclinic system. The melting-point of the anhydrous crystals is given as 156–157° and the density as d_4^{18} (vac.) 1·665. Citric acid is optically inactive. The dissociation constant of the first hydrogen atom is $8{\cdot}2\times10^{-4}$ at 18° (Kolthoff and Bosch, Rec. trav. chim. 1928, **47**, 558) and the values for the second and third hydrogen atoms are given as $1{\cdot}77\times10^{-5}$ and $3{\cdot}9\times10^{-7}$ respectively. The ordinary crystallised acid dissolves in about half its weight of boiling water. Aqueous solutions have, according to Gerlach (Z. anal. Chem. 1869, **8**, 295), the sp.gr. at 15° given in the table at head of next column.

Acid %	Sp.gr.	Acid %	Sp.gr.
1	1·0037	34	1·1422
2	1·0074	35	1·1467
3	1·0111	36	1·1515
4	1·0149	37	1·1564
5	1·0186	38	1·1612
6	1·0227	39	1·1661
7	1·0268	40	1·1709
8	1·0309	41	1·1756
9	1·0350	42	1·1814
10	1·0392	43	1·1851
11	1·0431	44	1·1899
12	1·0470	45	1·1947
13	1·0509	46	1·1998
14	1·0549	47	1·2050
15	1·0588	48	1·2103
16	1·0632	49	1·2153
17	1·0675	50	1·2204
18	1·0718	51	1·2257
19	1·0762	52	1·2307
20	1·0805	53	1·2359
21	1·0848	54	1·2410
22	1·0889	55	1·2462
23	1·0930	56	1·2514
24	1·0972	57	1·2572
25	1·1014	58	1·2627
26	1·1060	59	1·2683
27	1·1106	60	1·2738
28	1·1152	61	1·2794
29	1·1198	62	1·2849
30	1·1244	63	1·2904
31	1·1288	64	1·2960
32	1·1333	65	1·3015
33	1·1378	66	1·3071

A 25% solution boils at 101·8°, a 50% solution at 105·8°. The acid is very soluble in alcohol and moderately so in ether. At 15° the solubility of the crystallised acid in 100 parts of alcohol is as follows: in 80% alcohol 87 parts of the acid; in 90% alcohol 52·85 parts; in 100% alcohol 75·90 parts (Schiff, Annalen, 1860, **113**, 190; Bourgoin, Bull. Soc. chim. 1878, [ii], **29**, 244).

100 parts of anhydrous ether dissolve 9·12 parts of the crystallised acid (Lippmann, Ber. 1879, **12**, 1650).

Chemical Properties.—When heated to 175° citric acid is partially converted into *aconitic acid* (Crasso, Annalen, 1840, **34**, 56), the remainder losing water to form carbon dioxide and acetonedicarboxylic acid which immediately breaks down to carbon dioxide and acetone. Beyond 175° an oily distillate appears which yields crystals of *itaconic acid.* At still higher temperatures *citraconic anhydride* is formed as an uncrystallisable oil (Anschutz, Ber. 1880, **13**, 1541). When citric acid is digested with slightly fuming sulphuric acid (von Pechmann, Ber. 1884, **17**, 2542) or oxidised with potassium permanganate solution at 35° (Denigès, Compt. rend. 1900, **130**, 32) *acetonedicarboxylic acid* is formed. At higher temperatures potassium permanganate solution gives oxalic acid (Phipson, J.C.S. 1862, **15**, 142). By fusion with potassium hydroxide oxalic and acetic acids are formed (Liebig, Annalen, 1838, **26**, 158). Citric acid is fermented by numerous moulds, yeasts and bacteria (Kayser, Chem. Zentr. 1896, **1**, 583; Bruce, J. Biol. Chem. 1934, **107**, 119).

Salts.—Citric acid is tribasic and forms three classes of salts. The salts with the alkali metals are readily soluble in water; the neutral salts of the alkaline earths are only sparingly soluble. The *calcium* salt, $Ca_3(C_6H_5O_7)_2,4H_2O$, is less soluble in hot than in cold water and can be dried at 100° without loss of water of crystallisation. If the moisture content exceeds 10–12% calcium citrate is liable to decompose when stored at room temperatures. When precipitated in a crystalline state its solubility in water is 1 in 1180 at 14°, and 1 in 1730 at 90–100°. When thrown down in an amorphous condition the solubility is greater, 1 in 707 at 18°, and 1 in 1,123 at 100° (Warington, J.C.S. 1875, **28**, 939). Citric acid readily forms stable double citrates and hence the hydroxides of many metals are not precipitated by alkalis in the presence of citric acid. *Ferric ammonium citrate*, which is used for medicinal purposes, is prepared by evaporating a solution of ferric citrate in ammonia on glass plates, the red compounds contain 20·5 to 22·5% Fe, and the green 14 to 16% Fe.

Acyl Derivatives and Esters.—The *acetyl* derivative of citric anhydride is prepared by warming the acid with acetyl chloride on a water bath, dissolving it in lukewarm water and keeping *in vacuo* over concentrated sulphuric acid. The colourless syrup soon deposits shining crystals of *acetocitric acid* which are very soluble in water and melt at 138°–140° (Easterfield and Sell, J.C.S. 1892, **61**, 1005). *Methylene-citric acid* is prepared by heating citric acid with four times its weight of polymeric formaldehyde at 140°–160°, and allowing the melt to crystallise (Steinberg, Chem. Zentr. 1902, **1**, 299). The pure crystals melt at 208°. *Trimethyl citrate* is obtained by bubbling hydrogen chloride into a mixture of anhydrous citric acid and absolute methyl alcohol for 2 hours, then refluxing for 6 hours, and finally crystallising from water and puryfying by distillation. It melts at 75·5° and boils at 98°/0·2 mm. (Donaldson, McCleary and Degering, J. Amer. Chem. Soc. 1934, **56**, 459). In the same paper an account is given of the preparation of *propyl*, *butyl*, and *amyl dimethyl citrates* by the alcoholysis of trimethyl citrate in the presence of the corresponding alcohol and *p*-toluenesulphonic acid as a catalyst.

Detection.—Pure citric acid is easily recognised by the action of heat. It evolves an acrid odour and yields an oily distillate which forms crystals of itaconic acid on cooling (Stevens, Ind. Eng. Chem. 1924, **16**, 155). A solution of calcium chloride added to a neutral solution of citric acid produces no precipitate in the cold, but calcium citrate, $Ca_3(C_6H_5O_7)_2,4H_2O$, is thrown out of solution on boiling. Various suggested methods for the detection of citric acid in mixtures, depend on the insolubility of some of its metallic salts such as the calcium salt (Kunz, Analyst, 1900, **25**, 40), the barium salt (Broecksmit, J.S.C.I. 1920, **39**, 173A), and the lead salt (Fresenius and Grünhut, Analyst, 1913, **38**, 55). Others depend upon the formation of acetonedicarboxylic acid, which forms a sparingly soluble mercuric double salt (Denigès, Compt. rend. 1900, **130**, 32), gives acetone on boiling (Täufel and Schoierer, Z. Unters. Lebensm. 1936, **71**, 297) and which can be converted into insoluble pentabromoacetone by the action of potassium permanganate and bromine (Stahre, Analyst, 1895, **20**, 188). Thunberg (Biochem. Z. 1929, **206**, 109) describes a method using citric dehydrogenase from cucumber seeds and the methylene blue technique. It is difficult, however, to obtain concordant results by any of these methods. Precipitation of the metallic salts fails to distinguish citric acid unless it can be obtained fairly pure and in comparatively large quantity. Owing to the instability of acetonedicarboxylic acid even at room temperatures, methods depending on the formation of this compound are liable to give erratic results. Thunberg's method is only suitable for very small quantities of citric acid and requires special technique. The various methods have been reviewed by Elsdon and Lees (Analyst, 1933, **58**, 328) who consider that those depending on the formation of pentabromoacetone are the most satisfactory. They have found that a preliminary extraction with ether increases the sensitivity of Kunz's pentabromoacetone test (Analyst, 1916, **41**, 378) and recommend the following procedure: 200 g. of the substance to be tested are treated with 50 c.c. of ether in a stoppered flask for 20 hours. The ethereal solution is removed, evaporated to dryness, and the residue dissolved in 10 c.c. of water. This solution is treated with 1 c.c. of sulphuric acid (1 : 1), 0·3 c.c. of 37·5% potassium bromide solution, and 1 c.c. of 5% potassium permanganate solution. The mixture is heated for 5 minutes at 45°. Any trace of manganese dioxide is removed by the addition of ferrous sulphate solution containing sulphuric acid. If, after this treatment, any precipitate is present, citric acid is indicated. Under these conditions 0·1 g. of citric acid can be detected even in the presence of 100 g. of tartaric acid and 100 g. of sucrose.

MANUFACTURE.—For many years the main source of citric acid was the citrus fruits, chiefly lemons, pineapples, bergamots and limes, grown in Italy, Sicily, West Indies, California and Asia Minor. Since the development of the industrial fermentation processes an increasing quantity has been manufactured by these methods.

Lemon, Bergamot and Lime Juices.—Lemons are the principal source of citrus juice used for preparing citric acid and they are obtained chiefly from Italy and Sicily. The best and ripest fruits are chosen for export and the rest are used for the preparation of juice and essential oil. The fruits are cut in half and the peel, which contains the essential oil, is separated. The juice is pressed from the pulp and conveyed to a measuring tank. The pulp is often leached once or twice with water and pressed again before discarding. The juices are then allowed to undergo a short fermentation which precipitates some of the impurities, but involves no appreciable loss of citric acid. The juice is very difficult to filter unless this fermentation takes place. The filtered juice is a clear amber-coloured liquid containing about 4% of citric acid, and it can be used at once for the preparation of the acid. The juice is, however, usually concentrated until its sp.gr. is 1·24 and exported as such, in order to avoid the tariff imposed by many countries on the manufactured acid. Many manufacturers prefer to prepare the calcium salt, which is less costly to pack and transport. Besides free citric acid, citrates and certain other acids, such as malic, aconitic, formic, acetic, propionic acids, and their salts are usually present in citrus juices. The acidity does not, therefore, give the true content of citric acid. Citric acid in such liquors is estimated by a method described later, depending on the separation of insoluble calcium citrate. About 8% of the total acid in concentrated Sicilian lemon juice is not precipitable as calcium citrate. Concentrated bergamot juice has a similar sp.gr. to lemon juice, but a lower acidity, usually about 32% $C_6H_8O_7,H_2O$. About 13% of the total organic acid is not precipitable as calcium citrate. Concentrated lime juice has a sp.gr. of about 1·32 and an acidity of about 56% $C_6H_8O_7,H_2O$. About 10 to 14% is not precipitable as the calcium salt. The following table due to Grosjean (J.C.S. 1883, **43**, 333) gives analyses of commercial samples of concentrated lemon and other juices:

	Density	Acid (reckoned as citric acid) in oz. per gallon.		Proportion of precipitable to 100 of free acid.
		Free acid.	Total acid precipitable.	
Lemon Juice:				
Average of 65 samples	1·241	62·1	61·6	99·2
Sample A	1·240	65·8	59·7	90·7
Sample B	1·235	64·9	55·7	85·8
Bergamot Juice:				
Highest	1·235	47·9	48·5	101·4
Lowest	1·235	52·3	49·9	95·4
Lime Juice:				
Sample A	1·326	108·3	99·8	92·2
Sample B	1·205	59·2	53·9	91·1

Citric acid is usually prepared by way of the calcium salt. The juice, if concentrated, is diluted with water and run into a vat fitted with a steam heater and stirrer. The temperature is raised to 60°, and sufficient hydrated lime of high purity is added to neutralise 90% of the total acid estimated as citric acid. Chalk is then added to neutralise the remaining 10% of the total acid, and an excess of 7 kg. of chalk for every 3,700 litres of juice is also added. When the operation is completed a sample should no longer effervesce when more chalk is added. The liquid shows a slight acidity of about 0·15 to 0·20% $C_6H_8O_7,H_2O$. This acidity remains however great the excess of chalk. When the neutralisation is finished the mixture is boiled for 5 minutes and the precipitated calcium citrate washed with boiling water until the wash water has only a faint pale-straw colour. It is not advisable to neutralise completely with lime, as dark-coloured impurities are thrown down which are afterwards difficult to remove. Both the lime and the chalk should be as pure as possible, since alumina, magnesia, iron and phosphates interfere with the precipitation of citric acid, and cause appreciable losses of the acid. At a later stage in the process a washing of calcium sulphate takes place. This wash is used as a medium in which to suspend the calcium citrate. This mixture is slowly run into a vat containing sufficient sulphuric acid to decompose the citrate and to leave an excess of not more than 0·2% sulphuric acid. The mixture is kept agitated and the temperature raised to 55–57°. The temperature should at no time exceed 60°. The acidity is roughly gauged by adding 5 c.c. of 45% calcium chloride solution to an equal volume of filtered liquor. After placing on a steam bath for 5 minutes a faint precipitate of calcium sulphate should be noticeable. The acid liquor is drawn off from the precipitate of calcium sulphate which is then washed free from acid. The wash is used as mentioned above and the acid liquor is concentrated in open pans until it has a density of about 20°–25°Bé., and is then filtered from the calcium sulphate which separates during the concentration. The concentration is then completed in vacuum pans until the density is about 37°–38°Bé. The liquor is run into a vat and kept agitated while cooling. By this process, known as granulation, a heavy crop of small crystals of citric acid is obtained. The operation is a delicate one and requires to be done slowly. If the concentration is taken too far the result is a viscous liquid which will not granulate satisfactorily. The lumps of crystalline citric acid are allowed to drain before they undergo a light wash in a centrifuge. The mother liquor and the washings are concentrated again and a second crop of granulated material obtained. The process may be repeated a third time. When the liquor is too impure for further crystallisation it is known as "old liquor" and is returned to the neutralising tanks where it is treated like fresh juice.

The granulated citric acid is dissolved in water at 75° to give a solution of density 28°Bé., measured hot. A sample of the solution is filtered and a determination made of the charcoal required to decolourise the solution and of the quantity of calcium ferrocyanide to precipitate any iron and nickel present. The determination is carried out as follows: to several 25 c.c. portions of the clear filtered liquid varying amounts of $Ca_2Fe(CN)_6,12H_2O$ are added together with 0·5 g. of decolouring charcoal, and the mixtures heated on a steam bath for 10 minutes. The solutions are filtered and a drop of 1% $Ca_2Fe(CN)_6,12H_2O$ added to each. The sample which shows the least colour but still has a very faint blue, is used as the basis for calculating the amount of ferrocyanide to be added to the bulk. Usually enough ferrocyanide is added to precipitate about 90–95% of the iron and nickel present. The temperature is kept at 75° during the purification process. The filtered liquor is evaporated at low temperature until the density reaches 35°–36°Bé., measured at 50°. About 2 to 3 hours before this point is reached a sample is withdrawn and tested for free sulphuric acid, which, if present in large excess may appear in the finished crystals. For this test a sample of the filtered liquor is mixed with an equal volume of 45% calcium chloride solution and heated on a water bath. If more than a slight precipitate is formed a sufficient quantity of lime is added to reduce the excess to about 0·2% H_2SO_4. If lead-lined vessels have been used in the process appreciable amounts of lead may be present and can be removed at this stage together with any copper, tin and antimony. This is done by adding sulphuretted hydrogen water. By the end of the operation the sulphides will be precipitated and the excess of sulphuretted hydrogen boiled off.

The liquor is filtered clear and run into the crystallising vessels. If large crystals are required the liquor is kept perfectly still for about 3 to 5 days. When small crystals are required the liquor is kept in constant motion. After crystallisation is complete the liquor is drawn off and concentrated again. The process of crystallisation may be repeated as long as a satisfactory product results. The crystals are drained, washed in a centrifuge, and dried at room temperature, or in a low-temperature stove, before packing.

Manufacture by Mould Fermentation.—Wehmer (J.S.C.I. 1894, **13**, 275; B.P. 5620, 1893) first found that citric acid could be obtained from sugar solutions by means of certain moulds. No successful industrial process was developed, however, until Thom and Currie (J. Agric. Res. 1916, **7**, 1) showed that strains of the mould *Aspergillus niger* produce far more citric acid than Wehmer's original *Citromyces*. In a subsequent publication Currie (J. Biol. Chem. 1917, **31**, 15) laid the foundation for the commercial fermentation process by a careful study of the optimum conditions for the formation of citric acid by *Aspergillus niger*.

There are hundreds of strains within the species *Aspergillus niger*, differing but slightly in their morphological details, but showing wide variation in their biochemical characteristics. Different strains show great variations in their capacity for producing citric acid (Bernhauer, Biochem. Z. 1928, **197**, 278). Those are selected which give the highest yields of the acid and do not produce other acids when grown on small quantities of suitable medium. Protod'yakonov and Kresling (Proc. Inst. Sci. Res. Food Ind. Leningrad, 1935, (I) **3**, 3) state that the strains which give low yields form notched, darkly pigmented conidia and irregular-shaped heads, while those giving high yields form smoother heads. The latter are also more active in synthesising starch and form less fat in the mycelium (Kresling, *ibid.* 1935, (1), **3**, 130). The stock cultures must be sub-cultured at definite intervals. Unless precautions are taken the acid-producing capacity of the mould is liable to deteriorate. Stark (B.P. 302338) claims that the acid-producing capacity of the stock cultures on gelatine or agar media can be maintained if occasional growth cycles are introduced. This is accomplished by sub-culturing on to small quantities of solution similar to that used in the technical fermentation and next on to fruits rich in vitamins and containing organic acids, *e.g.* oranges, lemons, tomatoes, etc. Kresling and Shtern (Proc. Inst. Sci. Res. Food Ind. Leningrad, 1935, (I), **3**, 25) maintain activity by occasionally sub-culturing several generations of the mould on media containing 0·025 to 0·05 *N*-hydrochloric acid. In order to prevent unsuspected contamination of the stock cultures a method of bacteriological purification must be employed at definite intervals. Sucrose, invert sugar, glucose, maltose, and other sugars are suitable substrates for the fermentation. The best yields of citric acid are obtained, however, with sucrose. Currie considered the following medium to be most favourable for citric acid fermentation with *Aspergillus niger*:

	g. per litre.
Sucrose . . .	125–150
NH_4NO_3 . . .	2·0–2·5
KH_2PO_4 . .	0·75–1·0
$MgSO_4,7H_2O$.	0·20–0·25
HCl	4–5 c.c. of *N*/5-solution so that the p_H is 3·4–3·5.

The presence of metallic ions in the solution exercises a powerful influence on the growth of the mould and the production of acid. Steinberg (Amer. J. Bot. 1919, **6**, 330) gives a list of 17 elements, mainly heavy metals, which have been found to accelerate the development of *Aspergillus*. Although there has been considerable controversy about the stimulating action of many of these metals, Steinberg (J. Agric. Res. 1936, **52**, 439) concludes that iron, zinc, copper, manganese and molybdenum are all necessary for normal growth and that these elements cannot replace each other. The mould is very sensitive to traces of these metals and a strict control must be exercised on their presence. Thus Smith (J.S.C.I. 1936, **55**, 217T) states that the addition of 0·0001% of manganese to a culture solution containing small amounts of iron, copper and zinc caused a large increase in growth of the mycelium of *Aspergillus niger*. Individual strains show considerable differences as regards the optimum salt concentration for citric acid formation. Vasil'ev (Biochem. Z. 1935, **278**, 226) has shown that the different strains of mould which produce citric acid react differently from the addition of traces of zinc sulphate. The optimum nutrient salt concentration has to be found for each particular strain used, and for the type of vessel employed as the medium which gives the highest yields with small-scale fermentations is not necessarily the best when used on the large scale. Working with glass flasks Bernhauer, Duda and Siebenäuger (Biochem. Z. 1931, **230**, 475) obtained yields as high as 76.3% by wt. calculated on the sugar provided.

Various difficulties have been encountered when the citric acid fermentation has been attempted on a commercial scale. Even if the medium is sterilised before inoculation it is difficult to prevent infection by bacteria, yeasts and other fungi which interfere seriously with the citric acid fermentation. Certain organisms have a particularly unfavourable effect on *Aspergillus niger*. Yuill (Biochem. J. 1934, **28**, 222) describes a *Penicillium* which contaminates *Aspergillus niger* cultures. Fernbach and Yuill (B.P. 266415) add sufficient hydrochloric acid to the medium to bring the p_H to about 1·8 at which concentration the selected *Aspergillus niger* can grow to the virtual exclusion of invading organisms so that heat sterilisation can be omitted. A better yield of citric acid results when the inversion of sucrose takes place gradually and under the influence of the mould. The diminished hydrolysis of the sucrose and the reduced risk of metallic contamination of the medium from the reaction vessel are stressed in the above patent as advantages of the omission of heat sterilisation.

The fermentation is usually carried out in large, shallow vessels at a temperature of about 30° to 32°. The spores of the selected organism begin to germinate about 5 hours after they have been seeded on the surface of the medium. The mycelium develops deep folds and wrinkles which present a very large surface to the culture solution. Citric acid rapidly accumulates as soon as the mycelium has developed. The whole of the solution is constantly brought into contact with the mould by stirring or other means and controlled quantities of air are admitted to the cultures. After 8 to 12 days the solution is run off, and the mould pressed and leached. The liquors are then treated as above for the preparation of citric acid from citrus juices. Wells and Herrick (Ind. Eng. Chem. 1938, **30**, 255) report a yield of 63% by wt. on the sugar taken.

Whilst the highest yields are obtained using pure sucrose, citric acid can be obtained from a cheap source of raw material such as molasses, the yield being about 19 per cent. Cahn (Ind. Eng. Chem. 1935, **27**, 201) carries out the fermentation with *Aspergillus niger* on shallow layers of bagasse impregnated with a molasses mash. The layers of bagasse are about 1 to 1½ in. thick and are supported on iron screens which form the bottoms of shallow trays. Aeration can thus take place both from above and below. The trays are protected from the acid by painting with a Bakelite varnish.

The fermentation occupies about 36 hours to 4 days, and sterilisation of the mash and its protection from infection from foreign organisms are stated to be unnecessary. At the end of the fermentation the citric acid is leached from the bagasse carrier, which can be used over and over again.

METHODS OF ANALYSIS.—*Commercial Citric Acid.*—Accurately weigh out 3 g. of the sample, dissolve in about 100 c.c. of water, and titrate with *N*-sodium hydroxide using thymol blue as indicator. Each c.c. of *N*-sodium hydroxide is equivalent to 0·07003 g. of $C_6H_8O_7,H_2O$. The "British Pharmacopœia," 1932, gives the following tests for purity: heat 1 g. of the powdered sample in a boiling water bath with 10 c.c. of concentrated sulphuric acid for 1 hour; not more than a faint yellow colour is produced (absence of tartaric acid and of readily carbonisable substances). Dissolve 2 g. in 20 c.c. of a solution containing about 10% of NH_3 and 1 c.c. of 10% solution of calcium chloride, and allow to stand for 24 hours; the solution remains clear (limit of oxalic acid). Dissolve 2 g. in 40 c.c. of water and add 10 c.c. of dilute ammonia solution (as above) and 5 drops of 10% lead-free solution of sodium sulphide; the colour produced is at most only slightly deeper than that produced in a similar mixture containing in addition 1 c.c. of a 10% solution of potassium cyanide (limit of copper and iron). Dissolve 2·5 g. in water and add 1 c.c. of 10% barium chloride. Stir immediately with a glass rod and set aside for 5 minutes. The turbidity produced is not greater than that produced by adding 2·5 c.c. of *N*/100 sulphuric acid to a similar solution without the sample (limit of sulphates). Arsenic can be conveniently determined by the Gutzeit method and should not be present in quantities greater than 1 part per million. Lead is determined by dissolving in water 7 g. (primary solution) and 2 g. (auxiliary solution) of the sample; 10 c.c. of a solution of lead nitrate containing 0·001% of lead are added to the auxiliary solution. Each solution is made alkaline with a lead-free solution containing 10% of NH_3, and then 1 c.c. of 10% lead-free potassium cyanide is added. If the solutions are turbid they are filtered. The two solutions are diluted to 50 c.c. and 2 drops of a 10% lead-free solution of sodium sulphide are added to each and thoroughly mixed. If the the colour in the primary solution is greater than that in the auxiliary solution the sample contains more than the limit of 20 parts of lead per million. The proportion of lead in the sample can be determined by observing the quantity of the dilute solution of lead nitrate which must be added to the auxiliary solution in order that, after dilution to 50 c.c., there may be equal colours produced on the addition of 2 drops of the sodium sulphide solution. On incineration the sample should not leave more than 0·05% of residue.

Citrus Juices and Acid Liquors.—The acidity is determined by titration using thymol blue or phenolphthalein as indicator. Combined organic acids are estimated by neutralising a measured quantity of the sample with sodium hydroxide, evaporating to dryness, and gently igniting. The ash is dissolved in a known quantity of standard acid, boiled and filtered. The excess of acid is determined by titration with alkali. The alkali added when neutralising the sample, subtracted from the alkalinity of the ash, gives the amount of alkali corresponding to the bases of the organic salts. From this figure the amount of combined organic acid can be calculated.

Citric acid is usually estimated by Warington's method (J.C.S. 1878, **28**, 934) or a modification thereof. Warington proceeds as follows: 15–20 c.c. of unconcentrated lemon juice, or about 3 c.c. of concentrated juice, are exactly neutralised with sodium hydroxide. The solution is diluted to 50 c.c. and heated to boiling in a salt or glycerin bath and sufficient calcium chloride solution added to precipitate all the organic acid present. The whole is boiled for half an hour and the precipitate collected on a small filter and washed with hot water. The filtrate and washings are concentrated to about 10–15 c.c. and the solution neutralised with a drop of ammonia if it has become acid. The second precipitate thus obtained is collected, the filtrate being used to transfer the precipitate on to the paper, which is washed with hot water. In very accurate estimations the concentration should be repeated and any further precipitate collected. The precipitates in their papers are then burnt at a low red heat and the neutralising power of the ash determined with standard acid and alkali. Each c.c. of *N*-acid corresponds to 0·070 g. of $C_6H_8O_7,H_2O$. Sometimes the first precipitate only is collected and, the conditions being standardised, allowance is made for the solubility of the calcium citrate.

Calcium Citrate.—Excess of chalk or lime is estimated by dissolving 5 g. of the sample in dilute standard hydrochloric acid in a covered beaker and then titrating with standard alkali. Citrate is estimated by gently igniting 2 g. of the sample and determining the alkalinity of the ash with standard acid and alkali. By deducting from the alkalinity of the ash that due to the chalk previously determined, the amount of base which has to be calculated as citrate is found. If other organic salts are present the citrate is dissolved in dilute hydrochloric acid and the citrate estimated by Warington's method as in the case of citrus juices.

Milk, Wine, etc.—Citric acid occurs only in small quantities in these substances. Milk contains about 1 to 4 g., and wine about 0·4 g. per litre. The methods of estimation are based on the same principles as those mentioned above in the section on "detection." There are no very simple methods of estimation and many of those described in the literature are unreliable. Lampitt and Rooke (Analyst, 1936, **61**, 654) have examined a number of the methods and recommend a technique for estimating citric acid with special reference to milk. Their method is carried out as follows: to 50 c.c. of milk serum (Lampitt and Bogod, Chim. et Ind. 1932, **26**, 777), or other solution containing citric acid, are added 10 c.c. of sulphuric acid (1 : 1), if not already added in the preparation of the solution, except for pure citric acid and milk serum, 10 c.c. of freshly prepared bromine water should also be added, and any precipitate formed from acetonedicarboxylic acid filtered off after standing for half an hour. 5% Potassium permanganate solution is added drop by drop from a burette with constant shaking until a brown precipitate persists, 10 c.c. being usually required for 0·1 g. of citric acid and 25 c.c. for a milk serum. The mixture is allowed to stand at room temperature for 1 hour, further potassium permanganate being added if the brown precipitate disappears. Sufficient 20% ferrous sulphate in 1% sulphuric acid is then added slowly until a pale yellow solution containing a white precipitate is obtained, and the mixture is cooled in an ice chest overnight. The precipitate is removed by filtration through a sintered glass crucible, the reaction flask being washed out with the filtrate to remove the last traces of precipitate, and the washings passed through the crucible. The precipitate in the crucible is then washed with 10, 10, and 5 c.c. of cold water. The crucible is dried to constant weight in a vacuum desiccator. The precipitate is dissolved out of the crucible with industrial spirit, followed by 20, 10, and 10 c.c. portions of ether. The crucible is again dried in the vacuum desiccator and weighed, the loss in weight being taken as pentabromoacetone.

$$\text{Citric acid, } C_6H_8O_7 = 0{\cdot}424\left(w + \frac{0{\cdot}005V}{100}\right), \text{ where}$$

w represents the difference in weight of the crucible before and after treatment with industrial spirit and ether, V the original volume of filtrate from the reaction mixture less the total volume of washings. Results show that citric acid up to 0·11 g. may be determined in the presence of lactose to within 2 mg.

B. T.

CITRON. The fruit of *Citrus Medica* L. Originally of oriental origin, citrons are now grown in Southern Europe and in California and Florida. The fleshy-walled fruit is not edible in the raw state but is well known as "candied citron." The rind of the citron melon (*Citrullus vulgaris*), a variety of the common water-melon, is also prepared in a candied form as a substitute for the true citron. The tough, bitter-flavoured fruit is halved and fermented in brine for 40–50 days, during which the bitter flavour is removed and the tissue softened. The salt is then washed away and the peel steeped in a series of syrups of increasing sugar content until the maximum adsorption of sugar has taken place. Sucrose syrups tend to give a hard peel, and an admixture of 35% of fructose is common. The composition of fresh and candied peel is given by Fellers and Smith (J. Agric. Res. 1936, **53**, 859):

	Fresh.	Candied.
	%	%
H_2O	88·6	18·8
Ash	0·44	0·5
Protein	0·15	0·16
Ether extract . . .	0·32	0·33
Crude fibre	1·09	1·37
Total sugars (as invert)	1·55	43·0[1]
Total carbohydrates .	9·4	78·8
CaO	0·09	0·06
P_2O_5	0·05	0·04
K_2O.	0·11	0·02
Fe, Cu, I	traces	

[1] Consisting of 28·1% glucose and 14·9% sucrose.

A. G. Po.

CITRON, ESSENTIAL OIL OF. This oil, also known as oil of cedrat, is expressed in Sicily from the peel of the fruit of the citron, *Citrus medica* Linn (Fam. Rutaceæ). Three varieties are known as the cedro, the cedrone and the cedrino. The cedro has a thick rind and hard flesh, the cedrone has abundant edible flesh, and the cedrino is a small fruit.

Composition.—The main constituents are limonene, citral, of which 5 to 6% is present, and a stearoptene identical with citraptene found in oil of lemon.

Characters.—A pale yellow oil, sp.gr. 0·850 to 0·852, opt. rot. at 20° +80°–81°, n_{D}^{20} 1·475. Citron oil of commerce is frequently a mixture of oil of lemon, oil of orange and oil of bergamot.

C. T. B.

CITRONELLA, ESSENTIAL OIL OF. The oil obtained by distillation from the grass *Cymbopogon Nardus* Rendle, which is grown principally in Ceylon, Burma and the Straits Settlements. Two varieties of this grass are found in Ceylon. The best quality, known as Maha Pengiri or Winter's grass, yields an oil containing a high percentage of acetylisable constituents, 80–90%, and is found in Burma and the Straits Settlements. The acetylisable constituents consist of geraniol and citronellal. The commoner variety, known as *Lena Batu*, yields the ordinary Ceylon oil, which contains 55 to 65% of acetylisable constituents, chiefly geraniol. Two or three harvests a year can be obtained under favourable conditions.

Constituents.—Geraniol, citronellal, camphene, depentene, limonene, borneol, nerol, farnesol, methyl heptenone, and an aliphatic sesquiterpene. Java oil contains, in addition, dicitronelloxide, methyl-eugenol and citronellic acid.

Characters.—Ceylon oil has sp.gr. 0·897 to 0·912, opt. rot. at 20° −6° to −14°, n_{D}^{20} 1·479 to 1·485. Total acetylisable constituents 57 to 62%. Soluble in 10 volumes of 80% alcohol. The best oils (so-called plantation oils) are clearly soluble in 3 to 4 volumes of 80% alcohol and remain clear with 10 volumes. Inferior oils become turbid with 3 to 4 volumes of 80% alcohol, clearing somewhat with 10 volumes. Such oils may contain 10–15% of petroleum. The solubility test on which London contracts are based requires that the oil shall be soluble in 10 volumes of 80% alcohol with only slight turbidity, and with separation of oily drops on standing 24 hours at 15·5°C.

Java oil has sp.gr. 0·885 to 0·900, opt. rot. at 20° −2° to −5°, n_{D}^{20} 1·468 to 1·473. Total acetylisable constituents not less than 85%, determined by the method of the "British Pharmacopœia" for the determination of free alcohols in essential oils, but using the formula

$$\frac{7\cdot707n}{\text{weight of acetylated oil}-0\cdot021n}$$

$$=\text{Percentage of acetylisable constituents,}$$

where n=number of millilitres of $N/2$-alcoholic potassium hydroxide solution consumed during the saponification of the acetylated oil.

Citronellal Content.—The Ceylon oil contains only 6–8% of citronellal and the determination is not usually carried out in commercial practice. For the Java oil, however, the determination of citronellal is of importance, and the method adopted is as follows:

Weigh accurately about 2 c.c. of the oil in a stoppered tube and place in a freezing mixture. Add about 10 c.c. of a N-hydroxylamine hydrochloride solution, prepared as below, and cooled to −10°, and titrate immediately with N-alcoholic **KOH**, adding the alkali slowly, a few drops at a time, taking great care to avoid going beyond the orange colour. Continue the titration as long as a red colour develops, then allow to stand at laboratory temperature for one hour and complete the titration to the full yellow colour. Each c.c. of N-alcoholic potash is equivalent to 0·076 g. of citronellal.

Preparation of N-Hydroxylamine Hydrochloride Solution.—Dissolve 6·95 g. of pure hydroxylamine hydrochloride in 95 c.c. of pure 90% (by volume) alcohol; add 10 drops of a 0·2% solution of pure methyl orange in 60% alcohol, and adjust to the full yellow colour of the indicator with $N/2$-alcoholic potash and make up to 100 c.c. with 90% alcohol.

The percentage usually present is 30 to 40. Both oils are used for soap scenting, and the Java oil is employed as a source of geraniol and citronellal.

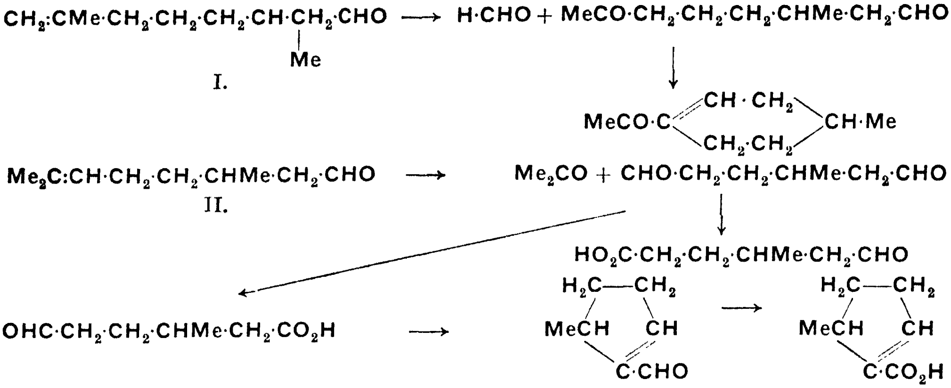
C. T. B.

CITRONELLAL. The aldehyde, *citronellal*, $C_{10}H_{18}O$, knownalso as *rhodinal*, although it is valued as a perfume, does not occur very widely distributed in nature. The dextrorotatory form, b.p. 205–206°, d^{20} 0·855, n_{D} 1·448, $[\alpha]_{\mathrm{D}}$ +12·3°, is the main constituent of Ceylonese citronella oil from *Cymbopogon Nardus*, and it is found also in certain eucalyptus oils; the lævorotatory aldehyde has been isolated from Javanese citronella oil and also from the oil from *Pinus Jefferyi*. For identification of the aldehyde the *semicarbazone*, m.p. 85°–88°, may be used, but a more characteristic derivative is *citronellyl-β-naphthocinchonic acid*, m.p. 225°, prepared by the condensation of the aldehyde with β-naphthylamine and pyruvic acid (Doebner, Ber. 1894, **27**, 2024). For the isolation of citronellal the compound which it forms with sodium bisulphite may be utilised, but care must be taken in its decomposition since the aldehyde is very susceptible to the action of alkalis.

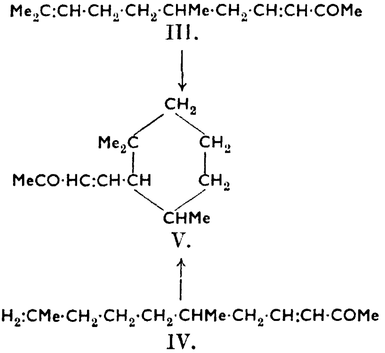
The constitution of citronellal was established by the extended investigations of Harries and his collaborators (Ber. 1901, **34**, 2981; 1908, **41**, 2187; Annalen, 1915, **410**, 8) on the oxidation of the aldehyde and its dimethyl acetal with ozone. They showed it to be a mixture of the two aldehydes represented by (I) and (II), degradation products of both these forms being obtained as indicated in the scheme at the head of the next page.

Since citronellol (*q.v.*) gives on oxidation citronellal (Tiemann and Schmidt, Ber. 1897, **30**, 33), the synthetic methods adopted for the preparation of this alcohol apply also to the aldehyde. On catalytic hydrogenation citronellal yields the saturated aldehyde *dihydrocitronellal* (Paal, G.P. 298193) or the saturated alcohol (von Braun and Kaiser, Ber. 1923, **56**, [B], 2271). On oxidation with silver oxide *citronellic acid* is obtained, the *dl*-form of which occurs in camphor oil (Rochussen, J. pr. Chem. 1922, [ii], **105**, 124) and probably also in the oil from *Calythrix Tetragona* (Penfold, Ramage and Simonsen, J. Proc. Roy. Soc. New South Wales, 1935, **68**, 80).

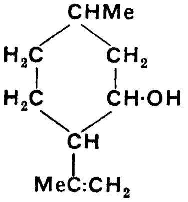
Citronellal condenses readily with acetone



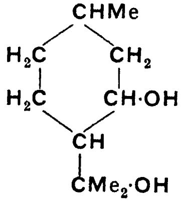
in the presence of alkali to yield *dihydro-pseudoionone* (III) and (IV) (Haarmann and Reimer, G.P. 75128; Rupe, Ber. 1900, **33**, 857) which on ring closure yields *dihydroionone* (V). This ketone has a refreshing odour and finds application in perfumery.



Cyclic derivatives may be prepared also very readily from citronellal itself. As was shown by Tiemann and Schmidt (Ber. 1896, **29**, 913; 1897, **30**, 27) it yields on digestion with acetic anhydride *isopulegol acetate*, which can be hydrolysed to the *alcohol* (VI). The alcohol is formed also by the action of dilute sulphuric acid (Barbier and Léser, Compt. rend. 1897, **124**, 1308; Horiuchi, Mem. Coll. Sci. Kyoto, 1928, **11**A, 171), formic and phosphoric acids (Prins, Chem. Weekblad, 1916, **14**, 627). With sulphuric acid the *glycol* (VII) is also formed.



VI.



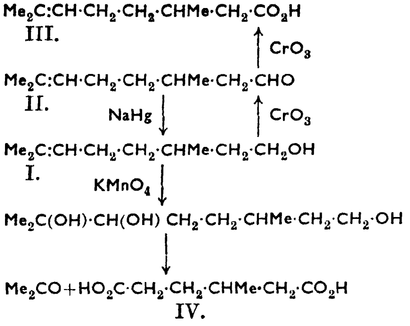
VII.

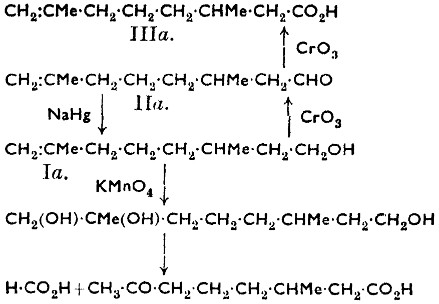
J. L. S.

CITRONELLOL. The alcohol *citronellol*, $C_{10}H_{20}O$, finds a wide application in the manufacture of perfumes and occurs in a number of essential oils, such as rose oil (from *Rosea damascena*), geranium oil (from *Pelargonium odorantissimum*) and in both Ceylon and Java citronella oils. It is identical with the alcohols known as *rhodinol*, *reuniol*, *roseol*. The natural alcohols are optically active and the following constants have been observed: *d*-citronellol (from Java citronella oil), b.p. 103°/5 mm., d^{15} 0·8604–0·8629, n_D^{15} 1·4565–1·45791, $[\alpha]_D$ +2·7°–2·3°; *l*-, b.p. 114–115°/12 mm., d^{22} 0·856–0·862, n_D^{20} 1·45609–1·4561, $[\alpha]_D$ −4·2°. The alcohol can be identified most readily by the preparation of the *allophanate*, m.p. 105–106° (Grignard and Doeuvre, Compt. rend. 1928, **187**, 270; Doeuvre, Bull. Soc. chim. 1929, [iv], **45**, 352).

The problem of the structure of citronellol has formed the subject of a prolonged controversy now only of historic interest. Since it is formed by the reduction of citronellal (II or II*a*) with sodium amalgam (Dodge, Amer. Chem. J. 1889, **11**, 465; Tiemann and Schmidt, Ber. 1896, **29**, 903) it must be a primary alcohol, and this is confirmed by its oxidation to citronellal with chromic acid, when at the same time citronellic acid (III and III*a*) and *iso*pulegol are formed (Tiemann and Schmidt, Ber. 1897, **30**, 32). On oxidation with potassium permanganate followed by chromic acid, acetone, formic, and β-methyladipic acids (IV) are obtained. The intermediate stages of the oxidation are shown in the scheme given at the head of the next page (Kotz and Steche, J. pr. Chem. 1924, [ii] **107**, 197).

There can be no doubt that citronellol is a mixture of the two alcohols represented by (I) and (I*a*) the actual percentage composition of the mixture being dependent upon the source or prior treatment of the alcohol. In a careful series of experiments Grignard and Doeuvre (*l.c.*) have shown the alcohol from four different sources, (*a*) from Java citronella oil, (*b*) from the reduction of citronellal, (*c*) from citronellal acetate, and (*d*) synthetic, from methylheptenyl bromide, to be a mixture in which the alcohol (I) predominates, the percentage varying from 81 to 72%. These values are based upon the yields of acetone and formaldehyde when citronellol is oxidised with ozone. The oxidation of citronellol with ozone was first studied by Harries and Himmelmann (Ber. 1908, **41**, 2187; Annalen, 1915, **410**, 8); subsequently Helferich and


Me₂C:CH·CH₂·CH₂·CHMe·CH₂·CO₂H
III.
CrO₃
Me₂C:CH·CH₂·CH₂·CHMe·CH₂·CHO
II.
NaHg
CrO₃
Me₂C:CH·CH₂·CH₂·CHMe·CH₂·CH₂OH
I.
KMnO₄
Me₂C(OH)·CH(OH) CH₂·CH₂·CHMe·CH₂·CH₂·OH
Me₂CO+HO₂C·CH₂·CH₂·CHMe·CH₂·CO₂H
IV.


CH₂:CMe·CH₂·CH₂·CH₂·CHMe·CH₂·CO₂H
IIIa.
CrO₃
CH₂:CMe·CH₂·CH₂·CH₂·CHMe·CH₂·CHO
NaHg
IIa.
CrO₃
CH₂:CMe·CH₂·CH₂·CH₂·CHMe·CH₂·CH₂OH
Ia.
KMnO₄
CH₂(OH)·CMe(OH)·CH₂·CH₂·CH₂·CHMe·CH₂·CH₂OH
H·CO₂H+CH₃·CO·CH₂·CH₂·CH₂·CHMe·CH₂·CO₂H

Sparmberg (Ber. 1931, **64**, [B), 104) have shown that the *hydroxyaldehyde*,

$$OHC{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2OH,$$

is formed also.

Citronellol has been synthesised in a number of ways: (*a*) by the reduction of ethyl geranate or ethyl citronellate with sodium and alcohol (Bouveault, Bull. Soc. chim. 1900, [iii], **23**, 458; Compt. rend. 1904, **138**, 1699; Barbier and Locquin, Compt. rend. 1913, **157**, 1114); (*b*) by the reduction of citronellal, and (*c*) by its conversion through its oxime into citronellic acid with subsequent reduction of the ester of this acid; (*d*) from methylheptenyl bromide (Grignard and Doeuvre, *l.c.*); (*e*) by the reduction of geraniol with aluminium amalgam which is said to be used technically (Ullmann, Encyclopädie der Technischer Chemie, **9**, 572). On catalytic hydrogenation citronellol yields the saturated alcohol (Paal and Amberger, G.P. 346949; Haller and Martine, Compt. rend. 1905, **140**, 1303).

J. L. S.

CITRONELLYL ESTERS. Citronellol (*q.v.*) forms a number of esters valuable as perfumes. They may be described as having floral and fruity odours, with, in general, rose and bergamot predominating. The following are the principal of these esters, with their approximate characters: *acetate*, b.p. 120°/15 mm., sp.gr. 0·901, n_D^{20} 1·4480; *butyrate*, b.p. 135°/5 mm., sp.gr. 0·891, n_D^{20} 1·4490; *propionate*, sp.gr. 0·895, n_D^{20} 1·4455. Citronellyl formate, benzoate, cinnamate, and valerianate are also prepared and used as perfumes to a small extent.

E. J. P.

CITRULLINE, $C_6H_{13}O_3N_3$, an amino-acid found in water-melon *Citrullus vulgaris* by Wada (Proc. Imp. Acad. Tokyo, 1930, **6**, 15; Biochem. Z. 1930, **224**, 420). It is formed by the action of putrefactive bacteria on arginine (*q.v.*) (Ackermann, Z. physiol. Chem. 1931, **203**, 66), and yields ornithine on alkaline hydrolysis (Wada, Proc. Imp. Acad. Tokyo, 1932, **8**, 367), and when perfused through the dog's stomach produces both arginine and ornithine. Citrulline has m.p. 220°–222°, is optically inactive and forms a violet *copper* salt, decomp. 257°–258°. The constitution α-amino-δ-carbamidovaleric acid,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}COOH,$$

has been confirmed by synthesis from arginine by way of ornithine, dibenzoylornithine, δ-amino α-benzamidovaleric acid and δ-carbamido-α-benzamidovaleric acid (Wada, *l.c.*).

CIVET. Civet is the most obnoxious of the animal perfume materials, having a revolting odour. When very highly diluted, however, its odour becomes pleasant, and its fixative properties in perfumes are very pronounced. It is a secretion from the perineal glands forming a deep pouch in the posterior part of the abdomen of the civet cat. The functions of the civet pouch are not definitely known, but it is probable that the repellent odour is a means of protection, or possibly its functions are those of sexual attraction. Practically the whole of the world's supply comes from Abyssinia. The cat which yields most of the civet is *Viverra civetta*, a wild animal which becomes fairly tame on keeping in captivity, except when the civet is being extracted. The cats are kept in long cages in which they cannot turn round, and their legs are secured and the civet extracted from the pouch with a small horn spoon. The secretion is greater if the animals are teased and irritated for a short time. There are other species of civet cats, but they are not of commercial importance. Civet is a substance of the consistency of honey, of a yellowish to brown colour, with a powerful fæcal odour. It is packed in bullocks' horns secured with a leather cap. The horns contain from 25 to 60 oz. Owing to its high price it is frequently adulterated. A genuine civet should have the following characters:

Loss at 100°—not exceeding 25%.
Mineral matter—not exceeding 2%.
Acetone extract—65 to 80%.
Alcohol extract—45 to 65%.
Ether extract—11 to 24%.
Chloroform extract—not exceeding 6%.

The acetone, alcohol, ether, and chloroform extracts should have the following acid and ester values:

	Acid value.	Ester value.
Acetone extract . .	85–115	25–50
Alcohol extract . . .	110–150	20–53
Ether extract . . .	8–26	55–90
Chloroform extract . .	6–40	75–170

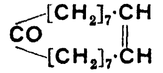
The acetone extract should not melt completely below 40° and the saponification value should be from 130 to 155. The principal adulterants of civet are petroleum jelly, lanoline, butter and banana pulp. The following table is given by Schimmel & Co. (Report, 1921, 60) as showing the characters of a number of adulterated samples of civet:

Civet (Adulterated).

No.	Alcohol extract.				Ether extract.				Chloroform extract.				Residue, %	Water, %	Ash, %	Mode of adulteration.
	%	A.V.	E.V.	S.V.	%	A.V.	E.V.	S.V.	%	A.V.	E.V.	S.V.				
1	28·4	122·3	38·7	161·0	25·2	6·7	28·0	34·7	0·2	—	—	—	16·9	29·3	1·2	Vaseline, organic substance, water
2	30·6	119·3	31·2	150·5	29·2	10·5	38·9	49·4	2·0	8·4	111·9	120·3	15·4	22·8	1·0	Vaseline, organic substance, water
3	34·6	127·8	33·2	161·0	9·3	21·1	66·2	87·5	0·1	—	—	—	49·3	6·7	43·0	Talc
4	43·8	120·9	17·9	138·8	38·2	13·2	34·4	47·6	4·3	6·5	97·7	—	6·6	7·1	—	Vaseline
5	29·8	101·0	16·8	117·8	53·9	8·4	30·5	38·9	7·2	—	—	—	6·8	2·3	—	Vaseline
6	26·9	120·8	50·0	170·2	27·6	6·1	26·4	32·5	0·3	—	—	—	16·8	28·4	1·04	Vaseline, organic substance, water
7	28·3	130·6	39·6	170·8	23·2	18·2	40·6	58·8	0·5	—	—	—	17·6	30·4	—	Vaseline, organic substance, water
8	29·8	122·2	32·0	154·2	25·8	9·8	35·8	45·6	2·3	12·2	97·4	109·6	16·0	26·1	1·2	Vaseline, organic substance, water
9	41·4	—	—	—	41·6	—	—	—	3·4	—	—	—	5·8	7·8	—	Vaseline
10	41·5	119·1	36·9	156·0	12·5	28·0	56·0	84·0	0·5	—	—	—	20·2	25·3	1·5	Vaseline, organic substance, water
11	35·3	115·8	38·9	154·7	12·8	26·2	65·6	91·8	0·3	—	—	—	45·0	6·6	39·0	Talc
12	33·3	—	—	—	13·4	—	—	—	0·2	—	—	—	44·9	8·2	—	Organic substance
13	34·0	—	—	—	10·8	—	—	—	0·2	—	—	—	48·7	6·3	—	Organic substance
14	33·5	128·7	29·2	157·9	11·0	20·4	68·7	89·1	0·5	—	—	—	48·1	6·9	42·2	Talc
15	37·6	119·9	53·6	173·5	19·6	28·6	71·4	100·0	0·6	—	—	—	19·3	22·9	1·7	Vaseline, organic substance, water

The following publications should be consulted: E. J. Parry (Chemist and Druggist, 1902, **61**, 901; 1903, **62**, 871; 1904, **65**, 168); Burgess (Analyst, 1903, **28**, 101); Charabot and Hébert (Bull. Soc. chim. 1910, (iv), **8**, 687); Schimmel & Co. (Reports, 1921, 60; 1924, 99; 1930, 110); Nivière (Bull. Soc. chim. 1920, (iv), **27**, 794); and Bennett and Seaber (Perf. & Essent. Oil Rec. 1929, **20**, 14). Civet contains scatole, indole, ethylamine, propylamine, some free acids not identified, and a characteristic ketone which was described by Sack (Chem.-Ztg. 1915, **39**, 538) under the name zibetone, but which is now usually known as civetone, melting at 31°.

Civetone has the formula $C_{17}H_{30}O$. It has been completely synthesised by Ruzicka (Helv. Chim. Acta, 1926, **9**, 230) and shown to be a 17-carbon ring compound. Its constitution is as follows:



$$CO\begin{cases}[CH_2]_7\cdot CH\\ \quad\quad\quad\ \ \|\\ [CH_2]_7\cdot CH\end{cases}$$

E. J. P.

CLARIFOIL. Cellulose acetate transparent tissue.

CLARIT. A German activated earth.

CLAUSTHALITE, a mineral of the formula $PbSe$.

CLAVICEPSIN, $C_{18}H_{34}O_{16},2Aq.$, m.p. 91°, and 198° (anhydrous), is found in *Secale cornutum*; it is not hydrolysed by emulsin, but gives 2 molecules of glucose and 1 molecule of mannitol on acid hydrolysis (Marino-Zuco and Pasquero, Gazzetta, 1911, **41**, [ii], 368).

E. F. A.

CLAY (Fr. *Argile*; Ger. *Thon*). The term "clay" denotes certain earthy materials which possess the property of plasticity and which when heated to redness or higher become hard. Clays are the weathered products of silicate rocks, especially those of the felspathic type, and contain hydrated aluminium silicates. According to J. W. Mellor ("Comprehensive Treatise on Inorganic Chemistry," London, 1925, VI, 468) there are three recognised hypotheses on the conversion of felspathic rocks into clays. These are (1) the action of surface waters charged with carbon dioxide; (2) the action of water draining from peat bogs containing organic acids in solution; (3) the action of volcanic gases and vapours, that is, pneumatolytic action. In the normal weathering of granitic rocks, water, carbon dioxide and oxygen are the chief agents causing the breakdown. Ferrous compounds present in the rock are oxidised to hydrated ferric oxide, some of which may remain. The alkali and alkaline earth compounds formed are removed in solution, while the quartz is comparatively unaffected. Thus, as the result of this weathering, hydrated aluminium silicate, hydrated ferric oxide, quartz, together with a proportion of felspathic or micaceous material, remain. If the water attacking the granitic rocks contains organic acids, *i.e.* humic acids in solution, the action is more severe. In some cases the severity of the action has resulted in the breakdown of the hydrated aluminium silicate, hydrated alumina remaining. Such an action is known as *laterisation*. Certain important beds of highly aluminous earths, such as gibbsite ($Al_2O_3\cdot 3H_2O$), bauxite ($Al_2O_3\cdot 2H_2O$), and diaspore ($Al_2O_3\cdot H_2O$) are of lateritic origin. The natural deposits of clay are themselves extremely diverse in character and frequently very impure, owing to the action of the different natural agents and the opportunities which have occurred in geological time for such processes as the leaching out or infiltration of soluble salts, the classification according to particle size in streams, rivers, lakes and seas, the admixture with mineral or organic impurities, sedimentation, the consolidation by pressure or earth movements. The china clays of Cornwall have probably been formed by pneumatolytic action. In support of this it is pointed out that (1) the clay is often found at considerable depths in the body of the rock, (2) minerals containing boron and fluorine are often found associated with these clays.

The terms " primary clay " and " residual clay " are used for those clays which are found at the place of their formation. China clay is an example of this type. In general, primary clays are comparatively free from impurities other than quartz and undecomposed felspars. These impurities are removed by washing from commercial china clay. A " secondary clay " or " sedimentary clay " is one which has been transported, usually by water, and redeposited. Such transportation and redeposition may have taken place many times. The sedimentary clays obviously fall into the geological classification of sedimentary rocks.

In Great Britain, in the Carboniferous System, there occur clays of considerable economic importance. Thus, in the Middle and Lower Coal Measures fireclays, which form the basis of the refractory materials industry, are found. These clays are obtained in many districts, particularly Stourbridge, North Staffordshire, Yorkshire (Halifax, Leeds, Sheffield, etc.), Durham, and Lanarkshire. Besides the manufacture of firebricks, clays belonging to this class are used in the manufacture of drainpipes, glazed bricks, and sanitary fireclay ware. In the Upper Coal Measures of the Carboniferous System considerable deposits of a series of clays known as Etruria marls are found in North and South Staffordshire and the Ruabon district of North Wales. These clays, which may be fired " red " or " blue " according to the methods of firing adopted, are used extensively in the production of roofing tiles. The Keuper marls (clays) of the Triassic; the Lias clays, the Oxford clays and the Kimmeridge clays of the Jurassic; the Weald clay and the Gault of the Cretaceous, and certain Tertiary clays, are all used in the manufacture of building bricks. Ball clays, which are characterised by high plasticity and bonding power, are fine-grained, sedimentary clays of the Tertiary group. They are found at Newton Abbot (Devon) and Poole (Dorset), and together with china clay are used extensively in the pottery industry.

The Composition of Clay.—Most clays are composite bodies containing, in varying amounts, (1) hydrated aluminium silicates, (2) quartz, (3) ferruginous compounds, including limonite, siderite, pyrites, and nontronite, (4) alkaline earth compounds, (5) felspathic and micaceous substances, (6) carbonaceous matter. The following ultimate analyses of some clays will illustrate this diversity of composition :

Table 1.—Analyses of Clays.

	China clay (Cornwall).	Ball clay (Devon).	Fireclay (Stourbridge).	Fireclay (Scotland).	Etruria marl (N. Staffs.).	Triassic clay (Birmingham).
	%	%	%	%	%	%
SiO_2	46·90	59·42	55·24	44·24	50·10	54·32
TiO_2	0·37	0·94	1·34	1·36	1·54	0·78
Al_2O_3	39·52	27·24	28·35	36·92	24·64	20·14
Fe_2O_3	0·30	0·62	2·25	2·16	10·72	6·32
CaO	0·25	0·47	0·40	0·22	2·10	5·71
MgO	0·16	0·22	0·22	0·14	0·46	3·21
K_2O	0·20	2·26	0·84	0·36	1·82	1·40
Na_2O	0·06	0·40	0·36	0·16	0·36	0·32
Loss on ignition . .	12·56	8·90	10·52	14·10	8·20	8·02
	100·32	100·47	99·52	99·66	99·94	100·42
Calculated Proximate Analyses.						
" Clay substance " .	98·1	60·9	67·6	90·90	—	—
Quartz	—	21·0	19·5	0·50	—	—
Felspathic matter . .	1·4	16·0	7·2	3·10	—	—

(The titanium, iron, calcium, and magnesium compounds are not included in the proximate analyses.)

Numerous attempts have been made to examine clays by the so-called method of rational analysis, the object being to determine by chemical means alone the amounts of " clay substance," quartz, and " felspathic matter " present in them. These efforts have not proved satisfactory. By making certain assumptions, chiefly that the " clay substance " has a formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and that the felspathic matter can be calculated as orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ (the total alkalis being considered as K_2O), a " proximate " analysis can be computed from the ultimate analysis of a clay. This is a useful device.

Kaolin or china clay is often regarded as the simplest form of clay. In early investigations all clays were assumed to contain a proportion of " clay substance," the composition of which approximated to that of china clay *i.e.* that given by the formula

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O.$$

J. W. Mellor (Trans. Ceram. Soc. 1917, **16**, 73) showed that a crystalline mineral—kaolinite—with the above formula could be isolated from china clay. He used the term "clayite" for the supposed non-crystalline "clay substance," which formed by far the greater proportion of clays he investigated. More recently C. S. Ross and P. F. Kerr (U.S. Geol. Survey, Prof. Paper 165E, 1931) concluded that the crystalline fraction of kaolin comprises at least three distinct minerals, kaolinite, nacrite, and dickite, all with the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$—thus explaining the anomalous results obtained by previous workers. They also emphasised the presence of the non-crystalline fraction. It is accepted in these days that other hydrated aluminium silicates may be present in clays. These include halloysite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$), allophane ($Al_2O_3 \cdot SiO_2 \cdot nH_2O$), montmorillonite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O + xH_2O$), beidellite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O + xH_2O$), pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$). It is interesting to note that there is a complete isomorphous series ranging from beidellite to nontronite

$$(Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O),$$

the latter being often found in clays. Further, the X-ray spectra of montmorillonite, beidellite, and pyrophyllite are practically identical. Montmorillonite and beidellite have been recognised as important constituents of the bentonites which are highly colloidal substances derived from the weathering of certain volcanic ashes (E. S. Larsen and E. T. Wherry, J. Washington Acad. Sci. 1925, **15**, 465). Recent investigations using X-ray methods have further indicated the crystalline nature of most of the hydrated aluminium silicates associated with clay—particularly kaolinite, halloysite, beidellite, and montmorillonite.

R. E. Grim and R. H. Bray (J. Amer. Ceram. Soc. 1936, **19**, 307) have investigated the mineral constitution of thirteen ceramic clays of widely different properties. They paid particular attention to the colloid portion, which was in turn subdivided into $(-1+0{\cdot}1\mu)$, $(-0{\cdot}1+0{\cdot}06\mu)$, and $(-0{\cdot}06\mu)$ fractions. A centrifuge technique (R. H. Bray, R. E. Grim and P. F. Kerr, Bull. Geol. Soc. Amer. 1935, **46**, 1909) has been devised for this purpose. The different minerals were identified by optical study with the petrographic microscope and chemical analysis of the bulk sample and all fractions. X-ray diffraction photographs were also obtained on the colloidal fractions. The non-clay minerals such as quartz, mica, and glauconite were usually found mainly in the non-colloid portion. The clay minerals listed above constituted the colloid fractions, and generally one or two only were dominant for each type of clay studied. Somewhat similar results have been reported by C. W. Correns (Naturwiss. 1936, **24**, 117). It is interesting to record the fundamentally crystalline character of practically all the inorganic clay constituents of colloidal dimensions which these workers examined. One mineral occurring in the colloid fraction in most of the clays examined has not been identified so far. It is described as "sericite-like" and is apparently the same as that named "glimmerton" (mica clay) by K. Endell, U. Hofmann and E. Maegdefrau (Zement, 1935, **24**, 625). Grim and Bray have tentatively assigned to it the formula

$$2K_2O \cdot 3MO \cdot 8R_2O_3 \cdot 24SiO_2 \cdot 12H_2O$$

while Endell and co-workers state that it loses water continuously on heating between 200° and 600°C. Reviewing the evidence which they have collected, Grim and Bray have concluded that kaolinite, beidellite, montmorillonite, the sericite-like mineral, and halloysite are the most important clay minerals. According to them, many clays and shales do not appear to contain kaolinite at all.

Different ceramic properties are necessarily associated with the presence of these minerals in natural clays, but the effects are difficult to evaluate because of the influence of particle-size as well as the specific attributes of each mineral. In a roughly qualitative manner certain influences have been assigned. Thus, drying shrinkage and bonding strength increase with the content of beidellite. A characteristic of this mineral is its high base-exchange capacity; hence clays in which it is present in quantity will be highly sensitive to additions of electrolytes. Since alkalis and iron are commonly present in beidellite, clays containing appreciable quantities are apt not to be refractory, and there is a tendency towards red firing colours. Montmorillonite exerts an action similar to, but more pronounced than, beidellite. This can be appreciated when it is stated that montmorillonite is the essential constituent of most bentonites. Kaolinite under comparable conditions confers less bonding power and induces less shrinkage than does beidellite. It contains no constitutional alkalis, has few adsorbed basic ions, and its aluminium is not isomorphously replaced by iron. Thus, it is generally refractory and white burning. Both china clay and ball clay are kaolinitic clays; the high bonding power of the latter results from high subdivision of the particles coupled with the presence of organic material and some beidellite. The sericite-like mineral, often a dominant constituent of shales, under similar conditions of fineness tends to yield lower values for the unfired properties than kaolinite. As it contains potash and its aluminium is probably replaceable by iron, it is not refractory and is often red-burning.

THE ACTION OF HEAT ON CLAYS.—The effect of heat on clays was early examined by H. L. Le Chatelier (Z. physikal. Chem. 1887, **1**, 396). He observed a retardation in the heating curve of crystalline kaolinite at about 550°C. and an acceleration in the rate of rise of temperature at about 1,000°C. J. W. Mellor (Trans. Ceram. Soc. 1910, **9**, 94; 1911, **10**, 161; 1914, **13**, 83) made similar observations. Thus when "clay substance" is heated, an endothermal reaction occurs in the neighbourhood of 500°C., and an exothermal reaction between 900° and 1,000°C. Table 2 gives the thermal data for these reactions obtained by W. M. Cohn (J. Amer. Ceram. Soc. 1924, **7**, 359, 474, 548; Ber. deut. Keram. Ges. 1923, **4**, 55); A. E. MacGee (J. Amer. Ceram. Soc. 1926, **9**, 206); H. E. Simpson (J. Amer. Ceram. Soc. 1927, **10**, 897).

TABLE 2.

Substance.	Heat absorption on 1 g. (500°C.).	Heat evolution on 1 g. (950°C.).	Authority.
China clay	93 cals.	16 cals.	W. M. Cohn
Georgia kaolin	127 „	23 „	A. E. MacGee
Zettlitz kaolin	92 „	16 „	W. M. Cohn
Halle clay	93 „	11 „	W. M. Cohn
Fireclays	82 „	18 „	H. E. Simpson

Quantitative values for the above reactions have also been obtained by L. Navias (J. Amer. Ceram. Soc. 1923, **6**, 1268). In addition to the above thermal reactions S. Satoh (Sci. Rep. Tôhoku, 1923, (3), **1**, 157) concluded from a study of his heating curves that a very weak exothermic reaction takes place between 1,170° and 1,220°C.

The endothermic reaction observed with many clays in the region of 500°C. is associated with the evolution of the combined water or water of constitution. Varying results for the dehydration temperature of clays have been obtained, owing probably to the influence of the rate of heating. Thus, H. S. Houldsworth and J. W. Cobb (Trans. Ceram. Soc. 1923, **22**, 111) found that kaolin lost a small proportion of combined water on heating to 400°C. in about 7 days, but the main loss occurred between 420° and 450°C. It has been further indicated by R. Rieke (Sprechsaal, 1911, **44**, 637) that kaolin is not completely dehydrated at 600°C. C. S. Ross and P. F. Kerr (U.S. Geol. Survey, Prof. Paper, 165E, 1930) have indicated that pure kaolinite loses the largest part of its total combined water at about 450°C., dickite at about 575°C., and nacrite at about 650°C. Some clay minerals such as montmorillonite lose a considerable amount of their water at temperatures of 140°C. This water is probably different in nature from the water of constitution of kaolinite. Rehydration below 400°C. is considered to be due to the presence of colloidal constituents such as colloidal silica, colloidal alumina, or " allophanoid " substances. Ross and Kerr have suggested that the water removed on heating the beidellite and montmorillonite minerals is composed of " zeolitic " water, water of constitution, and adsorbed water. The chemical change which proceeds at about 500°C. also influences the combination of the alumina, rendering this constituent soluble in hydrochloric acid. J. W. Mellor and A. D. Holdcroft (Trans. Ceram. Soc. 1910, **9**, 94) consider that these observations are best explained by assuming the complete breakdown of the clay molecule into free silica, free alumina, and water. This view is supported by G. Tammann and W. Pape (Z. anorg. Chem. 1923, **127**, 43). Other views which have been suggested assume that the water of combination is set free, leaving $Al_2O_3{\cdot}2SiO_2$—leverrierite (W. Vernadski, Trans. Ceram. Soc. 1923, **22**, 398; and F. W. Clarke, Bull. U.S. Geol. Survey, 1895, **125**, 32)—or that an aluminium silicate of the type $Al_2O_3{\cdot}SiO_2$, together with free silica, is formed (J. Samoilov, Trans. Ceram. Soc. 1924, **23**, 338); whilst J. M. Knote (Trans. Amer. Ceram. Soc. 1910, **12**, 350) suggested the formation of two compounds, $Al_2O_3{\cdot}SiO_2$ and $Al_2O_3{\cdot}3SiO_2$.

In the neighbourhood of 850° the alumina becomes much less soluble in hydrochloric acid. The chemical change occurring between 850° and 1,060° has been attributed by J. W. Mellor to the polymerisation and crystallisation of the free alumina. Numerous observations on the formation of a crystalline alumino-silicate in clay bodies at high temperatures have been made. J. W. Mellor and A. Scott (Trans. Ceram. Soc. 1924, **23**, 327), on firing mixtures of kaolin and alumina between 1,200° and 1,700°, and afterwards treating the material so formed with hydrofluoric acid, obtained an insoluble residue approximating to the composition of sillimanite ($Al_2O_3{\cdot}SiO_2$) after the treatment at the lower temperatures, and mullite

$$(3Al_2O_3{\cdot}2SiO_2)$$

after the treatment at the higher temperatures.

The more recent work on the X-ray spectra of kaolin after heating to various temperatures has led to different conclusions. J. W. Mellor, W. Bragg and G. Shearer (Trans. Ceram. Soc. 1924, **23**, 314) state that when kaolinite is heated at about 550° the crystal pattern of kaolinite disappears and is not replaced by any new pattern, and thus the products of decomposition are devoid of crystalline structure. The results obtained by J. F. Hyslop (Trans. Ceram. Soc. 1925, **24**, 402) are somewhat different. The pattern obtained from china clay heated at 450° for 5 hours showed no marked change in the position of the kaolinite lines as obtained with the raw clay, but showed a decrease in intensity. After heating to 550°C., a faint pattern unlike that of alumina or any of the silica modifications appeared, becoming more definite at 600° and persisting at 850°C. This pattern was considered to be due to a compound of the formula $Al_2O_3{\cdot}2SiO_2$. After heating to 950°C., the pattern disappeared and was replaced by that of mullite ($3Al_2O_3{\cdot}2SiO_2$), which became more intense after heating to 1,050°C. With clays containing quartz, heating at the higher temperature caused the transformation of some of the quartz to cristobalite. J. F. Hyslop and H. P. Rooksby (Trans. Ceram. Soc. 1928, **27**, 93, 299) in a later investigation confirmed the above observations and in addition noted the appearance of a pattern, associated with crystalline alumina, after heating to 870°C. This phase disappeared after heating to 1,060°C. Many other investigations have indicated the appearance of mullite in clays fired to 1,050°C. or over. In most cases the presence of either cristobalite or tridymite—crystalline modifications of silica—has also been observed, some of which, after heating to very high temperatures, appears to pass into solution.

As already stated, most clays—other than china clay—used in the manufacture of refractory materials, building bricks, and other ceramic products are impure; in fact, some so-called clays contain less than 40% of "clay substance." This variation in the constitution of clays has its influence on the firing operation, the principle of which is to produce from a satisfactorily manufactured and dried clay shape a finished product possessing strength, shape, and such general or particular properties as fit it for its subsequent duties. Since hardly any two clays are the same in their behaviour towards firing, it must seem that the firing operation is not capable of much standardisation. Nevertheless, in considering the industrial firing operation, three definite periods of importance stand out. These are (1) the water-smoking period, ranging in normal firing from ordinary temperatures to about 250°C. ; (2) the oxidation period, ranging from 500° to 850°C.; (3) the vitrification range from 800° to the finishing temperature (*v.* A. T. Green, Trans. Ceram. Soc. 1927, **26**, 110). The water-smoking period is concerned with the expulsion of the water from the setting of the dried goods in the kiln, for, even after drying, the ware may contain up to 5% of water. In a kiln, full of heavy clay ware weighing 100 tons, this means that up to 5 tons of water may require to be eliminated. The inadequate appreciation of the control of this stage of the firing may not only set up severe strains and ultimate weakness in the final product but may also cause the control of the subsequent heat work to be seriously impaired. The oxidation period is mainly concerned with the elimination of carbonaceous matter, the oxidation of iron compounds, the breakdown of carbonates, sulphides, and other compounds, together with the decomposition of the clay molecule with the evolution of the water of constitution. During this stage many properties are determined. In the firing of bricks made from fireclay, carbonaceous matter and the iron compounds may either individually or together form " black cores " or " discoloured centres." The nature of the iron oxide which forms during firing depends upon the amount of oxygen available, the steam in the atmosphere and the rate of rise of temperature. In a limited supply of oxygen or in an excess of steam, ferrous compounds will be formed or maintained, while under strongly oxidising conditions, during the oxidation period, ferric compounds will be formed. The formation of " black cores " is often due to a deficiency of air during this stage, so that the carbonaceous matter of the clay is incompletely oxidised, and the iron remains in the ferrous condition forming a fusible ferrous silicate, which causes an early vitrification in the interior of the product. It is obvious, therefore, that the rate of rise of temperature during this period must be most carefully controlled and that the steam formed owing to the decomposition of the clay must be quickly eliminated, the kiln atmosphere thus having to be carefully regulated.

J. W. Mellor (Trans. Ceram. Soc. 1933, **32**, 403) has brought forward an explanation of certain colour effects due to iron oxide in buff-coloured fireclay bricks. It is based on the dissociation of the clay at 500°–600°C. into free silica and alumina and the disposition of the alumina to enter into solid solution with ferric oxide, and thereby produce a paler buff colour, at the same time conferring greater stability on the ferric oxide. The alumina, which, for any cause, may not have taken up the iron into solution (*e.g.* the iron being present as FeO or Fe_3O_4 owing to reducing conditions), is less liable to do so at temperatures over 800°C. On this basis a rational explanation of bricks with red cores and buff exteriors, and with buff cores and red exteriors, has been given.

The final period of firing is that associated with the vitrification of the product. Vitrification may be defined as the progressive partial fusion of the various mineral constituents of a clay, chiefly including the felspathic, micaceous, calcareous, and ferruginous substances, which is governed by, amongst other factors, the composition of the body as a whole, the size of the grain, and the desired texture of the ware. In fact, the object of the heat work during this period is the production of a suitable amount of vitrified or glassy material, which will surround the remaining particles and fill the insterstices to an extent dependent on the properties desired in the finished product. Naturally, then, vitrification, which is the partial fusion of certain of the constituents of the clay resulting in the coherence of the mass, depends on both chemical and physical factors. Physically, the grain size has a very considerable influence, for the greater the surface per unit area, the greater the interaction taking place. Chemically, the nature and amount of the fluxes present in the clay determine the rate and extent of the reactions possible. With fireclays the rate of vitrification is slow up to temperatures in the neighbourhood of 1,200°C. Many clays used in the manufacture of building bricks such as Oxford clays or Triassic clays show rapid vitrification at temperatures ranging from 900° to 1020°C. The range of temperature during which the actions involved in vitrification take place to any appreciable extent varies very considerably. With calcareous and highly micaceous clays this range is very small, being of the order of 50°, but with good fireclays the range during which appreciable effects are evident is often from 1,280° to 1,400°C. Here, then, is the crux of successful heat work, for it is essential to produce such an amount of vitrified matter which gives strength with resilience without affecting the shape of the product. Thus, J. W. Mellor has pointed out that the chemistry of the firing of clay wares is the chemistry of arrested reactions.

The measurement of (1) the change in porosity and (2) the linear contraction of a clay when fired to different temperatures can give guiding information concerning its behaviour during the vitrification. Contraction data are very useful in the manufacture of clay products which must be made reasonably true to size and shape. F. R. Ennos and A. Scott (Mem. Geol. Survey, Fireclays, 1925, **28**, 3) have given the porosity-temperature curves of many clays. They divided clays into a number of groups depending on the rate of decrease of porosity with temperature. Such a classification gives some indication of the maturing conditions necessary to produce a satisfactory product. In certain instances the clays show a steady decrease in porosity with temperature of firing, pointing to a prolonged vitrification, whereas with others there is obviously a temperature at which the clay starts to vitrify with great rapidity.

It has already been indicated that siliceous fireclays contain free quartz varying in grain size from sub-microscopic particles to grains of appreciable magnitude. After firing, much of this quartz may remain as such embedded in the matrix or supporting structure of the fired body. Depending on the duration of the fire, the size of the grain, and the nature of the matrix, some of the quartz may be transformed into cristobalite. It does not follow, however, that a high silica content in the original clay will produce high quartz or cristobalite content in the fired product. The quartz, at least some of it, may go into solution in the viscous flux during vitrification and remain in this state after cooling. When silica is thus dissolved, the characteristic reversible expansions associated with the presence of quartz or cristobalite disappear.

THE PLASTICITY OF CLAYS; SUSPENSIONS.—The plasticity of clay may be defined as that property which enables it to change its shape under the action of a deforming stress without cracking and without any tendency to resume its original form on the removal of the stress. In certain theories plasticity has been attributed to (1) the size and shape of the particles; (2) the physical properties of the water film surrounding the clay particles; and (3) the colloidal contents of the clay. Clays differ widely in plasticity, but in general such clays as ball clays and bentonites possess the greatest plasticity. Certain fireclays, in their natural condition, are shaly, and require fine grinding with water to develop plasticity. Some clays, *e.g.* certain aluminous fireclays and china clays, show little plasticity, these being technically described as " lean " or " short " as opposed to ball clays which are termed " fat." The amount of water required to produce maximum workability varies widely with the clay, " short " clays, in general, requiring less water than " fat " clays. J. W. Mellor (Trans. Ceram. Soc. 1922, **21**, 95) has shown that the water content required to produce maximum workability decreases with the pressure applied to the clay in working. In the plastic, stiff-plastic, and semi-dry processes of manufacture this fact is utilised. A clay which requires, say, 26% of water for the plastic method may be successfully moulded under high pressure (200 kg. per sq. cm.) with a water content of, say, 6%. Although no satisfactory method of obtaining an absolute measure of plasticity exists, many empirical tests have been used. In works practice, plasticity is usually gauged by " feel," a manual treatment of pulling, bending, twisting and wedging being used. Laboratory tests include the Vicat needle test (*v.* Vol. II, p. 144*a*), the measurement of the flow of clays through dies and tubes, and the measurement of the effects of tension and compression on clays containing controlled amounts of water. A highly plastic clay has, in many cases, a high tensile strength in the dried state. This fact is sometimes used as the basis of an indication of plasticity. E. C. Bingham (" Fluidity and Plasticity," New York, 1922) has developed a formula for the plastic behaviour of solids in which the plastic flow is related to the applied stress, yield value and the viscosity coefficient. T. W. Talwalkar and C. W. Parmelee (J. Amer. Ceram. Soc. 1927, **10**, 670) have studied the stress-strain relation of clays by means of the torsion testing of cylinders of clay and have found the Bingham equation satisfactory. In these investigations important technical characteristics of different clays have been indicated. E. O. Wilson (J. Amer. Ceram. Soc. 1936, **19**, 115) has also investigated plasticity by means of a torsion machine giving stress-strain relationships. The results indicate that plasticity is due to the presence of stable viscous water films held on the surface of the particles; these in turn depend on the shape and surface activity of the particles. Clays show the highest plasticity because in addition to a plate-like structure they have a high surface activity. The older plate-structure and the colloid theories are thus blended. R. E. Wilson and F. P. Hall (J. Amer. Ceram. Soc. 1922, **5**, 916), G. W. Scott Blair and E. M. Crowther (J. Phys. Chem. 1929, **33**, 321), G. W. Scott Blair (J. Rheology, 1930, **1**, 127; Trans. Ceram. Soc. 1931, **30**, 138) have reported valuable investigations which have a bearing on the fundamental conception of the plasticity of clays.

The workability of a wet clay may be increased by storing in a cool, damp place for a period of time. This process, known as " souring," gives a more even distribution of water throughout the mass and makes the clay tougher. Souring may be hastened by the addition of small quantities of certain organic substances, such as gums, tannin and humus, which favour the growth of certain bacteria. D. P. Glick (J. Amer. Ceram. Soc. 1936, **19**, 169) has studied the micro-organisms present in six types of clay. By comparing the properties of raw, aged and sterile clays he has shown that the presence of living organisms are contributory factors to the ageing of clays. Traces of some salts affect plasticity considerably, a small quantity of acid increasing the workability and strength, whereas the addition of alkali has an opposite effect. The plasticity and drying shrinkage may be decreased by the addition of non-plastic material, such as sand or fired clay material (grog), and by suitable blending of different substances bodies of varying degrees can be obtained.

Elutriation determinations show that 68–98% by weight of ball clays consists of particles smaller than 0·010 mm. diameter. H. G. Schurecht (J. Amer. Ceram. Soc. 1920, **3**, 355) found that an English ball clay contained 81% by weight of particles of size less than 0·0005 mm., whilst some English china clays contained only 5% of such particles. J. J. T. Schlœsing (Compt.

rend. 1874, **79**, 376, 473) succeeded in removing 1·4% of material of a colloidal nature from a certain clay, whilst J. W. Mellor (Trans. Ceram. Soc. 1922, **21**, 95) removed only 0·5% from another. In general, clays in suspension have an acid reaction, the p_H range according to F. P. Hall (J. Amer. Ceram. Soc. 1923, **6**, 901) being 3·10–7·37. Methods for the more accurate measurement of the particle size of clays have been put forward by A. H. M. Andreasen (Ber. deut. Keram. Ges. 1930, **11**, 249, 675), R. T. Knapp (Ind. Eng. Chem. 1934, **6**, 66), C. R. Amberg (J. Amer. Ceram. Soc. 1936, **19**, 207). The particles in a clay slip are negatively charged and can be deposited on an anode immersed in the clay slip. On suspending a clay in distilled water, the coarse particles settle out rapidly and the clay matter remains suspended for a length of time, the suspension containing particles smaller than 1·1 micron. This suspension is typically colloidal, and exhibits the Brownian movement, Tyndall effect, and cataphoresis. Additions of small quantities of acid to a clay slip cause flocculation; the acidity at which maximum flocculation occurs varies with different clays, according to Hall, from a p_H of 2·7 to 4·0. At this point the negative charge on the clay has been neutralised. Small additions of alkalis to a clay slip deflocculate the clay, the particles remaining suspended for a longer time, and the viscosity of the slip being reduced. If alkali be added in excess the viscosity is increased and the clay becomes flocculated. Thus, a casting slip, which ordinarily would be too thick to pour, can be successfully cast by the addition of controlled quantities of sodium silicate and sodium carbonate. Protective colloids such as gelatin and gum arabic, when added to a clay slip, may retard flocculation. Clays show selective adsorption; R. F. Geller and D. R. Caldwell (J. Amer. Ceram. Soc. 1921, **4**, 468) found that kaolins could adsorb sodium hydroxide to the extent of 1·25% on the dry weight of clay. Clays adsorb the basic ions of common salts, such as barium chloride and copper sulphate, in preference to the acid ions, whilst larger molecules of organic dyes, *e.g.* methylene blue, are also adsorbed. The mechanism of the reaction of clays slips to electrolytes has been discussed by G. I. Whitlatch (J. Amer. Ceram. Soc. 1931, **14**, 154), F. L. Clark (Trans. Ceram. Soc. 1933, **32**, 1), D. L. Peck and D. A. McLean (Ind. Eng. Chem. 1934, **6**, 85) and Z. W. Wolkowa (Kolloid.-Z. 1934, **67**, 280).

THE DRYING OF CLAY.—The shrinkage of clay during drying from the plastic state takes place in two principal stages. During the first the change in volume is equal to the volume of water lost; at a certain moisture content the clay becomes what is technically known as "leather hard," and at this point the clay particles are in contact and shrinkage practically ceases. During the second stage, from "leather hard" to dry, there is a small residual shrinkage attributed to loss of colloidal water and to closer packing of the clay grains. The transition from the first to the second stage is not sudden, there being an intermediate stage, which varies considerably with different clays.

Throughout the first stage, the rate of drying of a clay under constant conditions of temperature humidity is constant for unit area of surface, for during this stage there is a comparatively free flow of water to the surface. When the "leather-hard" stage is reached the free flow of the water to the surface is prevented, with a consequent falling off in the rate of drying. The shrinkage of the surface of a block of clay relative to the interior causes tensional strains to be set up in this superficial material. If drying is too rapid these strains become great enough to cause rupture and cracking. Care has to be taken that the greatest safe rate of drying is not exceeded. This safe rate depends on the texture of the clay or clay-ware.

One of the commonest methods of drying clay products in industry is by means of the hot floor. In this method the moulded articles are placed directly on the heated floor of a large shed. The chamber dryer consists of an enclosed space with means for heating and ventilating. In the tunnel dryer the goods are carried, and dried by steam pipes, hot gases, or other means. All types of commercial dryers are subject to very wide variations in design to meet the requirements of different branches of the clay industry. H. H. Macey (Trans. Ceram. Soc. 1934, **33**, 92), T. K. Sherwood and E. W. Cominge (Ind. Eng. Chem. 1933, **25**, 1, 118, 134) and F. H. Norton (J. Amer. Ceram. Soc. 1933, **16**, 86) have made useful contributions to the study of the drying of clays.

ANALYSIS OF CLAYS.—*General.*—The constituents determined in a normal clay analysis are silica, the oxides of aluminium, iron, titanium, calcium, magnesium and the alkali (sodium and potassium) oxides, together with the loss on ignition.

Many other constituents, *e.g.* the oxides of manganese and barium, sulphuric and phosphoric anhydrides, carbon dioxide and carbon, may have to be determined in special cases. The last two are included under the loss on ignition in a typical analysis. The limits of permissible error are usually taken to be ±0·5%, though different analysts work to different limits. If the analysis falls sensibly below 99·5% a qualitative examination must be made to identify the constituents which have escaped determination in the normal course of the quantitative work.

Sampling.—It is imperative to sample carefully the finely ground material, otherwise the analysis will not be a representative one and consequently of little value.

Determination of the Hygroscopic Moisture.—About 5 g. of the finely-ground material are dried in an air-bath or toluene oven at 105° to 110°C. until there is no further loss in weight (about 3 to 4 hours is generally sufficient). It is not usual to determine the hygroscopic moisture as normally the analysis is made on the dried sample.

Determination of the Loss on Ignition.—1 g. of the dry material is heated in a platinum crucible for 15 minutes over a small flame, then for 30 minutes over a good Méker burner, with the lid on for the last 10 minutes. The crucible and contents are cooled in a desiccator, weighed, again heated for 10 minutes over the Méker burner and the weight again checked after cooling.

Low results are usually due to the incomplete combustion of carbonaceous matter, whereas losses by spurting, produced by too rapid ignition (especially if carbonates be present), generally account for high results.

Determination of the Silica.—The ignited material in the platinum crucible is intimately mixed with 10 to 15 g. of anhydrous sodium carbonate. (Some analysts prefer to weigh out a fresh gram of the dry un-ignited material.) The lid is placed on the crucible and the mixture gently heated over a Méker burner and finally fused at a bright red heat until the contents are in a state of quiet fusion, usually 15 to 30 minutes are required. The crucible is allowed to cool on a clean unglazed tile; it is then half-filled with water and carefully heated over the tip of a small flame whereby the cake can usually be detached *en bloc* from the crucible. The cake and washings from the crucible are placed in a dry 250 c.c. basin, glazed on the inside only; after adding about 100 c.c. of water the basin is covered with a clock glass and 25 to 30 c.c. of concentrated hydrochloric acid are added from a pipette through the lip of the basin. When the first violent reaction is over the basin is warmed on a water bath until all action has ceased and the cake has disintegrated. Any drops on the underside of the clock glass are rinsed into the basin; the platinum crucible and lid are washed with hydrochloric acid and hot water and the washings also poured into the basin. The cake is now crushed to powder with a small agate pestle and the solution evaporated to dryness on a water bath until the smell of hydrogen chloride is no longer perceptible. When crystallisation has started the semi-solid mass must be repeatedly broken up with the end of a glass rod. The basin and contents are now baked in an air oven at 120°C. for 1 hour. The mass is moistened with concentrated hydrochloric acid and 75 c.c. of hot water added. After a few minutes' digestion the liquid is filtered and the residue washed with hot water until free from chlorides. The filtrate is returned to the basin, again evaporated to dryness, baked, digested with hydrochloric acid and hot water and filtered as in the first instance. The wet filter papers are transferred to a weighed platinum crucible and carefully dried and charred without ignition over a burner with a mushroom head. The carbon is then burnt off slowly over a Bunsen burner and the crucible and contents finally ignited for 30 minutes over a Méker burner, with the lid in position for the last 10 minutes.

The crucible is weighed and the result entered as " weight of crucible plus silica and residue." The silica contains traces of the oxides of aluminium, iron and titanium. Accordingly, it is treated with two or three c.c. of dilute sulphuric acid to prevent the subsequent volatilisation of titanic fluoride at red heat. About 15 c.c. of hydrofluoric acid are added, a few drops at a time, and, after placing the crucible eccentrically on a sand bath, the solution is slowly evaporated to dryness. When all the hydrofluoric acid has been expelled, the sulphuric acid can be rapidly and safely volatilised by heating the *rim* of the crucible, carefully, with the naked flame. The outside of the crucible is wiped free from sand; the crucible is then ignited for 5 minutes and weighed when cool. The result is recorded as " weight of crucible plus residue." The difference between the two weighings gives the amount of silica in the sample. Subsequently the ammonia precipitate is ignited in this crucible along with the silica residue.

Normally the weight of the silica residue does not exceed 10 mg.; a residue much in excess of this figure usually indicates the presence of barium sulphate or of relatively large quantities of titanic oxide in the material under analysis. In such cases the silica residue is fused with a small quantity of potassium pyrosulphate, the cake extracted and digested with dilute sulphuric acid until completely disintegrated. The solution is filtered; the residue, if any, washed free from sulphates, ignited and weighed as barium sulphate. The filtrate from the barium sulphate is added to the main bulk of filtrate from the silica.

The Ammonia Precipitate.—The filtrate from the silica is heated to 80° to 90°C. and 2 to 3 g. of solid ammonium chloride are added to it, followed by a slight excess of concentrated ammonia, drop by drop; the solution is simultaneously stirred well and then filtered, after standing for 5 minutes. If the clay contains manganese, which will be indicated by the green colour of the cake after fusion with sodium carbonate, 2 to 3 c.c. of bromine water are added to the solution before the two ammonia precipitations, otherwise the procedure is as described above. The precipitate is filtered and immediately washed four or five times with hot water; a hole is made in the apex of the filter paper and the precipitate washed back into the beaker from which it has just been filtered.[1] The filter paper is then washed free from chlorides and kept for ignition. The washings are collected in the beaker containing the precipitate. The precipitate is redissolved in a slight excess of concentrated hydrochloric acid; the solution, after dilution, heated to 80° to 90°C. and again precipitated by adding excess of ammonia, drop by drop with constant stirring. The liquid is filtered into the beaker containing the first filtrate and the precipitate washed repeatedly with small quantities of a hot alkaline solution of ammonium nitrate (2 to 3 g. per litre, made just alkaline with ammonia) until free from chlorides, but on no account must the ammonia precipitate be allowed to run dry.

The filtrate is evaporated to about 75 c.c. and 2 to 3 c.c. of ammonia are added and the excess boiled off. The liquid is filtered and the precipitate washed free from chlorides with the ammonium nitrate solution. The filtrate is kept for the determination of lime and magnesia. The three filter papers used in the ammonia precipitation are transferred to the crucible containing the silica residue and the papers are slowly dried and charred over a mushroom burner. The temperature is then raised until all the carbon is burnt off and the crucible finally heated, with the lid on, over a Méker burner until its weight is constant.

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[1] When the ammonia precipitate does not exceed 5%, only a slight excess of ammonia is added to the filtrate from the silica and the excess is boiled off. One precipitation only is necessary.

After weighing, the ignited oxides are very slowly dissolved in the crucible by fusion with 6 to 8 g. of pure fused potassium pyrosulphate.

The cake when cold is detached from the crucible and transferred to a porcelain basin and about 150 c.c. of water and 20 c.c. of concentrated sulphuric acid are added to it ; the crucible is well rinsed out with hot water and the washings poured in the basin. The mixture is heated on a water bath until all is dissolved; the solution is then cooled and diluted to 250 c.c. in a graduated flask to give the stock solution for the determination of iron and titanium oxides.

Determination of Ferric Oxide.—When the amount of ferric oxide does not exceed about 5%, a colorimetric process is used, while for larger amounts the determination is made by the ordinary permanganate process. The colour of the sample in the crucible after the determination of the loss on ignition is a good criterion as to which process is the better. For the colorimetric determination an aliquot portion of the stock solution, obtained from the pyrosulphate fusion, is diluted to 250 c.c. in a graduated flask to give the test solution. 25 c.c. are taken for a normal clay, or other materials, containing 1% or less of ferric oxide. 5 c.c. of the standard iron solution [1] are diluted to 100 c.c. in a graduated flask and a portion of this solution is transferred to a burette reading to 0·1 c.c., while a similar burette is filled with distilled water. Two small test glasses, of pure white glass, are respectively filled with a mixture of (*a*) 10 c.c. of the potassium thiocyanate [2] solution with 10 c.c. of a buffer solution of potash alum [3] and (*b*) 10 c.c. of the potassium thiocyanate solution with 10 c.c. of the test solution. The diluted standard iron solution is added from the burette to the potash alum solution and an equivalent amount of distilled water from the other burette to mixture (*b*), stirring thoroughly after each addition, until the tints in the two test glasses are the same. The tints are viewed against a neutral background by light transmitted through the sides of the glasses.

If more than 6 to 8 c.c. of the diluted iron solution are needed, errors are likely to result owing to the difficulty in judging the equality of tint in concentrated solutions of ferric thiocyanate. A weaker test solution must, therefore, be made by diluting 10 or 5 c.c. of the stock solution to 250 c.c.

Calculation.—Using 1 g. of material and the above-mentioned dilutions, the percentage of Fe_2O_3 is given by $V/8$, where V is the number of c.c. of diluted standard iron solution required to give a match in colour. If the 250 c.c. of test solution contains v c.c. of the stock solution, the percentage of Fe_2O_3 is $25\ V/8\ v$.

Determination of Titanic Oxide.—50 c.c. of the stock solution, obtained from the pyrosulphate fusion, are pipetted into a 100 c.c. graduated flask, 10 c.c. of 20 vols. hydrogen peroxide (free from fluorides) are added, and the mixture made up to the mark. 5 c.c. of standard titanium solution [1] and 10 c.c. of hydrogen peroxide are similarly diluted to 100 c.c. One of the test glasses used in the iron determination is about half filled with the solution to be tested. 10 c.c. of diluted standard titanium solution are pipetted into the other glass and water added to it from a burette, with frequent stirring, until the tints of the two liquids, compared as indicated in the previous determination, match.

Calculation.—If 1 g. of material be taken, with the dilutions given above, the percentage of TiO_2 is $25/(10+V)$, where V is the number of c.c. of water added to the 10 c.c. of diluted standard titanium solution to produce equality of tint. When v c.c. of the stock solution are diluted to 100 c.c. the percentage is :

$$1250/(10+V)v.$$

Determination of Alumina.—The weight of the ammonia precipitate less the weights of the ferric and titanic oxides and the filter ashes, used in the silica separation and the ammonia precipitations, gives the weight of alumina in the sample.

Determination of Manganese Oxide.—The percentage of manganous oxide, though rarely required in a clay analysis, can be estimated colorimetrically as follows.

A suitable quantity—say 5 c.c.—of a standard manganese solution [2] is pipetted into a 100 c.c. graduated flask and to it is added 10 c.c. of a 0·2% solution of silver nitrate and 1 g. of ammonium persulphate. The flask is heated on a water bath until a pink colour develops. By the time the contents of the flask have cooled to atmospheric temperature the colour, due to the permanganate produced in the oxidation, will have reached its maximum intensity. The solution is then diluted to 100 c.c. A brown precipitate on oxidation with the persulphate shows that insufficient silver nitrate has been used. In this case the solution is reduced by adding a few c.c. of sulphurous acid and reoxidised, after the addition of another 10 c.c. of the silver nitrate solution.

The stock solution, resulting from the pyrosulphate fusion, generally contains traces of chlorides which interfere with the determination. Hence 50 c.c. of it are boiled and the chlorides precipitated by the addition of silver nitrate. The solution is filtered and the precipitate washed, the filtrate and washings being collected in a 100 c.c. graduated flask.

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[1] *Standard Iron Solution.*—Dissolve 0·6040 g. of pure ammonium ferric alum in water, add 5 c.c. of concentrated sulphuric acid, and dilute the solution to a litre in a graduated flask. 1 c.c. = 0·0001 g. Fe_2O_3.

[2] *Potassium Thiocyanate Solution.*—97 g. (1 g. molecule) of the salt per litre.

[3] *Potash Alum Solution.*—0·05 g. of alumina, prepared by strongly igniting pure ammonium alum in a platinum dish, is fused with 5 g. of potassium pyrosulphate. The cold cake is extracted with water, 10 c.c. of concentrated sulphuric acid are added, and the solution is made up to 1 litre. This solution is used to counteract the effect of the aluminium sulphate in the test solution on the tint of the ferric thiocyanate.

[1] *Standard Titanium Solution.*—1 g. of pure titanic oxide is fused with 10 g. of potassium pyrosulphate. The cold cake is extracted with water and 20 c.c. of concentrated sulphuric acid are added. The mixture is gently warmed on a water-bath until the cake has completely dissolved, when the solution is diluted to 1 litre. 1 c.c. = 0·001 g. TiO_2.

[2] *Standard Manganese Solution.*—Dissolve 0·3145 g. of pure manganous sulphate, $MnSO_4,4H_2O$, in water, acidify the solution with a few c.c. of concentrated sulphuric acid, and dilute to 1 litre. 1 c.c. = 0·0001 g. of MnO.

10 c.c. of 0·2% silver nitrate and 1 g. of ammonium persulphate are added to the filtrate and the mixture warmed, cooled and diluted to the mark, as in the preparation of the standard permanganate solution. The tints of the standard and tests solutions are then matched exactly as described under the colorimetric determination of titanic oxide.

Calculation.—If the volume of water, taken to dilute the standard solution to the same depth of colour as the test solution, be v c.c., then, with the dilutions given above, the percentage of manganous oxide in the clay is $2{\cdot}5/(10+v)$.

Determination of Lime.—The filtrate from the ammonia precipitate is boiled for a few minutes with 1 to 3 g. of ammonium oxalate, and 5 to 10 c.c. of concentrated ammonia are added. After stirring well, the mixture is warmed on a water bath for 2 hours. The liquid is filtered, the precipitate washed two or three times and the filtrate reserved for the magnesia determination. A hole is made in the apex of the filter paper, the precipitate washed into the beaker from which it has been filtered, and redissolved by running a few c.c. of nitric acid over the filter paper into the beaker containing the precipitate. The filter paper, after washing, is rejected. The solution is boiled, again precipitated and warmed for 2 hours as before, after which it is filtered and the precipitate washed free from chlorides. The filtrate is added to that from the first precipitation. The precipitate is slowly charred and then ignited in a platinum crucible and finally heated over a Méker burner for 15 minutes, with the lid on the crucible for the last 5 minutes. The crucible, when cool, is rapidly weighed, again ignited for 5 minutes and the weight checked.

The percentage of lime is calculated from the weight of the residue less the weight of filter ash.

Determination of Magnesia.—The combined filtrate from the calcium oxalate precipitate is boiled with 1 to 2 g. of sodium ammonium phosphate; about 10 c.c. of concentrated ammonia are added and the solution is allowed to stand in the cold for at least 3 hours. The mixture is then thoroughly stirred and filtered and the precipitate washed once with cold water while the filtrate is rejected. A hole is made in the apex of the filter paper, the precipitate washed into the beaker from which it has just been filtered and the magnesium ammonium phosphate dissolved in a few c.c. of nitric acid, in the way described under the determination of lime. The solution is again precipitated, exactly as indicated above. The cold solution, after standing, is vigorously stirred, filtered through an ignited and weighed Gooch crucible and washed with a cold 10% ammonia solution until a few c.c. of the washings give no precipitate with a nitric acid solution of silver nitrate. The precipitate is dried, ignited, cooled, and weighed as magnesium pyrosulphate—the conversion factor to magnesium oxide being 0·3621.

Estimation of Alkali Oxides.—0·5 g. of the very finely powdered dry substance is thoroughly ground up with about 0·5 g. of ammonium chloride and 3 g. of calcium carbonate in an agate mortar, and the mixture transferred to a platinum crucible. The mortar is " rinsed out " with another gram of calcium carbonate and the " washings " added to the mixture in the crucible. After well stirring the contents with a glass rod, the crucible is heated over a small Bunsen flame for about 15 minutes, during which period the crucible is partly covered by the lid. When all the ammonium salts have volatilised the lid is placed in position and the lower third of the crucible heated to dull redness for 1 hour, but the cake must not be fused. The crucible is cooled, the cake transferred to a porcelain basin and the crucible thoroughly rinsed out into the basin with hot distilled water. After a few minutes the cake is gently powdered in the basin with an agate pestle; the mass is then digested with about 80 c.c. of hot water for 30 minutes, filtered and the residue washed with hot water until the washings occupy 120 to 150 c.c. The residue must be well washed, particularly if the amount of alkalis is large. The residue is rejected.

The filtrate is heated to 80° to 90°C. and 10 c.c. of ammonium carbonate solution [1] added to precipitate the lime. The liquid is filtered and the filtrate retained. A hole is made in the apex of the filter paper, the precipitate washed through into the beaker from which it was filtered and redissolved in about 5 c.c. of hydrochloric acid. The solution is boiled, a slight excess of ammonia and ammonium carbonate added and the liquid filtered into the vessel containing the first filtrate, the residue being well washed.

The combined filtrates are evaporated to dryness in a large platinum or silica dish. The dish is then covered with a clock glass and baked for an hour at 120°C. in an air oven. After removing the clock glass, the dish is ignited at a dull red heat until all the ammonium salts have volatilised. The cold residue is moistened with about 3 c.c. of ammonium oxalate solution, in order to precipitate the last traces of lime, and allowed to stand for 12 hours, after covering with a clock glass.

The mixture is filtered into a small platinum dish and the residue washed with ammonium oxalate solution. The filtrate is evaporated to dryness on a water bath, but, as the liquid may spurt during the early stages of the evaporation, the dish is covered initially with a clock glass and any liquid adhering to the glass is subsequently washed back into the dish. When dry, the residue in the dish is ignited and, when cold, the contents are moistened with a few drops of concentrated hydrochloric acid, again evaporated to dryness, ignited at a low red heat, cooled and weighed. The residue is then washed out with hot water into a small porcelain basin and the platinum dish again ignited and weighed. The difference in weight gives the weight of alkali chlorides.

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[1] *Ammonium Carbonate Solution.*—100 g. of pure, resublimed ammonium carbonate are dissolved in 100 c.c. of concentrated ammonia (sp.gr. 0·880) and the solution diluted to 500 c.c. with water.

Unless the reagents are definitely known to be free from alkalis, a blank determination of the alkalis as chlorides must be made on an equivalent weight of ammonium chloride and calcium carbonate. The amount found, if any, is deducted from the weight of mixed chlorides.

If the silicate contains appreciable quantities of sulphur compounds, the alkalis will be obtained partly in the form of sulphates at this stage. In such cases, before the final precipitation of the lime, the sulphates are converted to chlorides by the addition of a little barium chloride solution, followed by a few drops of ammonium carbonate solution to precipitate the excess of barium.

A few drops of perchloric acid (sp.gr. 1·20) are added to the liquid in the porcelain basin, at the rate of 6 c.c. per g. of mixed chlorides, and the solution evaporated almost to dryness on a water bath in an atmosphere free from ammonia fumes. 10 c.c. of water are added and the solution again evaporated to dryness. The residue is at once treated with alcohol wash liquor [1] and immediately filtered through a weighed Gooch crucible which has been previously heated to 120°C. for 1½ hours. The residue is washed with about 30 c.c. of the alcohol mixture and the crucible and contents dried for 1 hour at 120°C. and weighed. The weight of the precipitate represents potassium perchlorate which is calculated to potassium chloride and deducted from the weight of mixed chlorides to give the weight of sodium chloride. The equivalent amounts of the alkali oxides are then calculated.

The conversion factors are: potassium perchlorate to potassium chloride, 0·5381; potassium chloride to potassium oxide, 0·6317; sodium chloride to sodium oxide, 0·5302.

(This section on the analysis of clays has been written by Mr. H. V. Thompson, M.A.)

Literature.—The reader should consult original papers in the Transactions of the Ceramic Society (England), the Journal of the American Ceramic Society, Berichte der deutschen Keramischen Gesellschaft, etc. Other works are J. W. Mellor, "Comprehensive Treatise of Inorganic and Theoretical Chemistry," London, 1935, vol. VI (The Silicates); H. Wilson, "Ceramics," New York, 1927; Collected Writings of H. A. Seger, Easton, Pa., 1902.

A. T. G.

CLAY-IRON-STONE *v.* Chalybite.

CLAYITE. A name suggested by J. W. Mellor in 1909 for the non-crystalline variety of kaolinite, $H_4Al_2Si_2O_9$, of which china-clay and most other clays are largely composed. The same name had been earlier used by W. J. Taylor, in 1859, for an uncertain alteration product (of tetrahedrite?) composed of sulphur, arsenic, antimony, lead, and copper.

L. J. S.

CLEMATINE or BRILLIANT HELIOTROPE 2R (*v.* Azines).

CLEVEITE. A variety of uraninite, consisting of a uranate of uranyl, and oxides of lead and the rare earths. It occurs sparingly as small cubic crystals in pegmatite veins in the south of Norway; and is of interest as being the mineral in which terrestrial helium was first discovered. Hillebrand (Amer. J. Sci. 1890, [iii], **40**, 384) found that on decomposing the mineral with sulphuric acid, "nitrogen" was evolved. Ramsay (J.C.S. 1895, **67**, 1107) proved that the gas evolved was not nitrogen but helium. Only half the helium is evolved by heat alone, and, moreover, in some cases the disengagement of the gas is accompanied by considerable evolution of heat (Proc. Roy. Soc. 1898, **64**, 140). *See* Bröggerite.

L. J. S.

CLEVE'S ACIDS. 1-Naphthylamine-6 and 7-sulphonic acids.

CLIFTONITE *v.* Carbon, Graphite Vol. II, p. 315*a*.

CLOVE. The dried flower buds of *Eugenia aromatica* (Linn.) Baill. (Fam. Myrtaceæ), a native of Molucca, where it was also formerly cultivated, but now grown chiefly in Zanzibar and Pemba. The flower buds are white at first, becoming green and finally red, at which stage they are ready for collection and must be gathered immediately, the time of the year at which the harvest occurs being from August to December. The buds are air-dried and separated from their peduncles, which then form the clove stalks of commerce and these are used either as a source of oil or to adulterate the buds. Cloves vary in length from 10·0 mm. to 17·5 mm.; the largest and plumpest come from Penang and Amboyna, though very few of these reach the European market. The Zanzibar clove is brownish-black in colour, while that from Penang is reddish-brown, and the flower head of the Penang clove appears to be much more fully developed than that of the Zanzibar variety. The whole clove consists of a cylindrical calyx tube with four sepals at the top to which the flower bud proper is attached. Cloves possess an aromatic odour and a strong, spicy, and pungent taste. Fresh cloves should sink in boiled water, a distinction from exhausted cloves, which are frequently used for adulteration. They are used to a considerable extent as a spice and as an aromatic carminative, whilst the essential oil is largely used as a mild preservative. Corran and Edgar (J.S.C.I. 1933, 52, T149) have examined the preservative action, and find that mustard and cloves are far superior to all other spices, and better than the permitted amounts of sulphur dioxide or benzoic acid for preventing the fermentation of glucose by yeast.

Microscopic Appearance.—The chief microscopic characteristics are the numerous oil glands just beneath the surface of the calyx and the calyx teeth, and also in the petals. The pollen grains are tetrahedral and measure from 15 to 20μ in diameter. Rosette, but not prismatic crystals of calcium oxalate are present, and the buds contain no starch or sclerenchymatous cells. The bast fibres are broad, measuring about 50μ, and some idea of the proportion of clove stalk to bud may be obtained by counting the ratio of the bast fibres to the isodiametric sclerenchymatous cells in a powder. The stalks also contain prismatic crystals of calcium oxalate.

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[1] *Alcohol Wash Liquor.*—97 volumes of absolute alcohol, 3 volumes of water and 0·25 volumes of perchloric acid (sp.gr. 1·20). The solution should be kept in a stoppered glass bottle containing a few grams of finely powdered potassium perchlorate. The mixture is well shaken and filtered into a small dry washbottle immediately before use.

Chemical Composition.—The following table shows the approximate composition of clove buds and stalks :

	Buds.	Stalks.
	%	%
Moisture	5·0–8·3	8·7–10·2
Ash	5·3–7·6	6·9–8·0
Volatile oil	14·0–21·0	5·0–6·0
Fixed oil and resin. .	5·0–10·0	3·5–4·0
Protein	5·0–7·0	5·8–6·0
Crude fibre	6·0–9·0	13·0–19·0
Tannin	10·0–18·0	about 18

The principal constituent is the essential oil and this is probably determined most satisfactorily by the method of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435). The powdered buds are mixed with brine, distilled, and the vapours passed through the top of a condenser into a graduated tube, into which a small quantity of turpentine has been previously distilled to make the mixture lighter than water, the condensed water itself being returned to the distillation flask. An air inlet and outlet is provided by a side tube between the bottom of the condenser and the graduated tube.

Standards.—The " British Pharmacopœia " requires that cloves shall contain not more than 5% of clove stems and 1% of other foreign organic matter. The ash shall be not more than 10%, the acid-insoluble ash not more than 0·75%. The United States standard requires the buds to contain not more than 5% of stalks, not less than 15% of volatile oil, not less than 12% of quercitannic acid calculated from the oxygen absorbed by the aqueous extract, not more than 7% of ash, not more than 0·5% of acid insoluble ash, and not more than 10% of crude fibre.

Adulteration.—The chief adulterants are clove stems and exhausted cloves. Other adulterants, such as pimento and cereal products, have been detected.

T. McL.

CLOVENE *v.* Caryophyllene.

CLOVER. The name given to a number of leguminous crops grown for cattle-feeding. The true clovers are all species of *Trifolium* and include white clover (*T. repens*), red clover (*T. pratense*), alsike clover (*T. hybridium*), crimson clover (*T. incarnatum*), yellow suckling clover (*T. dubium*), mammoth red or zig-zag clover (*T. medium*), hop clover or hop trefoil (*T. procumbens*). Other " clovers " of agricultural value are yellow clover or yellow trefoil (*Medicago lupulina*), Bokhara clover or melilot (*M. alba*), sweet clover (*M. dentatus*), Japanese clover (*Lespedeza striata*), Soola or sulla clover (*Hedysarum coronarium*), various smaller vetches, etc.

The importance of clovers for cattle feeding lies in the high nitrogen and mineral matter contents. In addition, the soil in which they are grown is enriched in nitrogen as a result of the fixation of atmospheric nitrogen by the bacteria present in the nodules of the roots. In practice clovers intended for direct grazing are frequently grown in conjunction with " seed " grasses, or if required for winter feeding the unmixed clover is hayed. Average analyses of green clover and hay from (*a*) European, and (*b*) American sources are given below :

Green Clover.

	Water.	Protein.	Fat.	Soluble carbo-hydrates.	Fibre.	Ash.
	%	%	%	%	%	%
T. repens (*a*) . . .	81·5	4·4	0·8	6·9	4·3	2·1
T. pratense (*a*) . . .	79·0	3·4	0·7	9·4	5·9	1·6
T. pratense (*b*) . . .	70·8	4·4	1·1	13·5	8·1	2·1
T. hybridium (*a*) . .	81·8	2·8	0·7	7·0	6·2	1·5
T. hybridium (*b*) . .	74·8	3·9	0·9	11·1	7·4	2·0
T. incarnatum (*a*) . .	81·5	2·8	0·7	7·0	6·1	1·9
T. procumbens (*a*) . .	80·0	3·5	0·8	8·4	5·7	1·6

Clover Hay.

	Water.	Protein.	Fat.	Soluble carbo-hydrate.	Fibre.	Ash.
	%	%	%	%	%	%
T. repens (*a*) . . .	9·7	15·7	2·9	39·3	24·1	8·3
T. pratense (*a*) . . .	16·5	13·5	2·9	37·1	24·0	6·0
T. pratense (*b*) . .	15·3	12·3	3·3	38·1	24·8	6·2
T. hybridium (*a*) . .	16·0	13·6	3·1	34·5	25·7	7·1
T. hybridium (*b*) . .	9·7	12·8	2·9	40·7	25·6	8·3
T. incarnatum (*a*) . .	16·7	12·0	2·4	35·5	26·2	7·2
T. procumbens (*a*) . .	16·0	15·4	3·4	33·2	24·5	7·5
T. medium (*b*) . . .	21·2	10·7	3·9	36·6	24·5	6·1
Lespedeza striata (*a*) .	9·1	13·7	4·0	47·5	21·6	4·1
Lespedeza striata (*b*) .	11·0	13·8	3·7	39·1	24·0	8·5

Of the total nitrogen content of clovers as much as 40–50% may be in non-protein or amide forms in young plants. In mature plants 85–90% of the nitrogen is present as protein.

In New Zealand and elsewhere the presence of cyanogenetic glucosides in clovers has caused some anxiety. According to the investigations of Doak (New Zealand J. Agric. 1935, **51**, 159) poisoning of cattle or even any ill effect on milk flavour is likely to be of rare occurrence. Armstrong and Horton (Proc. Roy. Soc. 1913, B, **86**, 262) detected an enzyme capable of hydrolysing cyanogenetic glucosides in certain varieties of wild but not of cultivated white clover.

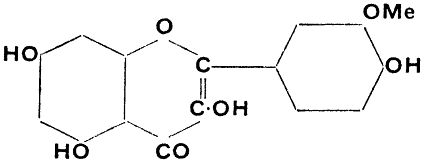
Wolff's analyses of the ash of clovers include the following, expressed as percentages of the dry matter.

	Total ash.	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
T. pratense . . .	6·83	2·20	0·14	2·41	0·74	0·07	0·67	0·21	0·16	0·27
T. incarnatum . .	6·08	1·40	0·52	1·92	0·37	0·12	0·43	0·15	0·99	0·22
T. hybridium . . .	4·76	1·32	0·15	1·62	0·60	0·02	0·48	0·20	0·19	0·26
T. repens	7·16	1·21	0·54	2·31	0·72	0·17	1·01	0·58	0·30	0·26

A. G. Po.

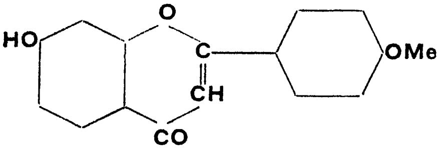
CLOVER FLOWERS. It has long been known that clover flowers dye a yellow colour on aluminium mordanted fabrics, and in the past they were employed to a minor extent for dyeing purposes. Three varieties have been chemically examined: *Trifolium pratense*, *T. incarnatum*, and *T. repens*.

Trifolium pratense.—According to Power and Salway (J.C.S. 1910, **97**, 231) the flowers known as the "common red clover" contain, in addition to iso*rhamnetin*:



and a *glycoside of quercetin*, m.p. 235°, numerous other phenolic substances which are described below. These appear to be closely allied to the colouring matters of the flavone group.

Pratol, $C_{15}H_8O_2(OH)(OCH_3)$, colourless needles, m.p. 253°, readily soluble in hot aqueous sodium carbonate and sodium hydroxide with a pale yellow coloration, yields a *mono-acetyl* derivative, feathery needles, m.p. 166°. Robinson and Venkataraman (J.C.S. 1926, 2344) observe that pratol closely resembles and is very probably identical with 7-hydroxy-4′-methoxyflavone:



m.p. 262° (*acetyl* derivative, feathery needles, m.p. 167°–168°), prepared by heating resacetophenone with anisic anhydride and sodium anisate and hydrolysing the product.

A *compound*, $C_{16}H_{10}O_7$, thin yellow plates, m.p. about 280°, is soluble in alkalis with a yellow colour and gives with sulphuric acid a solution exhibiting a brilliant green fluorescence. It contains a methoxyl group and forms a *tetra-acetyl* compound, colourless, glistening prismatic needles, m.p. 145°–147°.

Pratensol, $C_{17}H_9O_2(OH)_3$, feathery needles, m.p. 210°, dissolves in alkali carbonates yielding yellow solutions, and with alcoholic ferric chloride gives a greenish-black coloration. *Triacetypratensol*, colourless, slender needles, melts at 189°. Robinson and Shinoda (J.C.S. 1925, **127**, 1973) suggest that pratensol may be a trihydroxystyrylchromone related to apigenin.

A *phenolic substance*, $C_{15}H_7O_3(OH)_3$, colourless needles, m.p. 225°, is soluble in alkali hydroxides forming colourless solutions, and gives with alcoholic ferric chloride a dark green coloration. The *acetyl* derivative, silky needles, melts at 209°.

The glycoside *trifolin*, $C_{22}H_{22}O_{11},H_2O$, pale yellow needles, m.p. about 260° (decomp.), is soluble in alkalis with an intense yellow coloration, and dissolves in sulphuric acid forming a yellow solution which rapidly develops a brilliant green fluorescence. When hydrolysed it yields rhamnose and *trifolitin*, $C_{16}H_6O_2(OH)_4$, slender yellow needles, m.p. about 275° (decomp.). Alkalis dissolve trifolitin with an intense yellow colour, alcoholic ferric chloride gives a dark green coloration, and alcoholic basic lead acetate an orange-yellow lead salt. It contains no methoxyl group and is unaltered when heated for several hours with 30% aqueous potassium hydroxide. It does not appear to belong to the flavone group, and differs from these by the fact that it does not give an oxonium salt with sulphuric acid and only with difficulty a potassium compound by treatment with alcoholic potassium acetate. It may possibly consist of a tetrahydroxyphenylnaphthaquinone. The *tetra-acetyl* compound, colourless silky needles, when rapidly heated melts at 116°, resolidifies at a higher temperature, and finally melts at 182°.[1]

The glycoside iso*trifolin*, $C_{22}H_{22}O_{11}$, pale yellow needles, m.p. about 250°, is isomeric with trifolin, and when hydrolysed yields, similarly to the latter, trifolitin. Though in general behaviour it is very similar to trifolin, it is much more soluble in alcohol, and does not appear to be identical with this glycoside.

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[1] Both in its melting-point and that of its acetyl derivative there is a marked resemblance between trifolitin and kaempferol.

In addition to these compounds, the flowers contain salicylic acid, coumaric acid, myricyl alcohol, $C_{31}H_{63}OH$, heptacosane, $C_{27}H_{56}$, hentriacontane, $C_{31}H_{64}$, sitosterol, $C_{27}H_{46}O$, trifolianol, $C_{21}H_{34}O_2(OH)_2$, palmitic, oleic, linoleic, and *iso*linolenic acids.

Trifolium incarnatum.—A considerable difference is exhibited between the constituents of the " carnation or crimson clover flowers " and those of the *T. pratense* or " common red clover." According to Rogerson (J.C.S. 1910, **97,** 1004) these flowers contain pratol, quercetin, and a glucoside of quercetin termed *incarnatrin,* $C_{21}H_{20}O_{12},3H_2O$, yellow prismatic needles, m.p. 242°–245°. Incarnatrin dissolves in sulphuric acid, forming a green fluorescent solution, and when hydrolysed yields quercetin and glucose. It is isomeric but not identical with the quercimeritrin of Perkin (J.C.S. 1909, **95,** 2181).

In addition to these substances the flowers yield furfuraldehyde, benzoic, and salicylic acids, a trace of *p*-coumaric acid, incarnatyl alcohol, $C_{34}H_{69}OH$, hentriacontane, a phytosterol, $C_{27}H_{46}O$, and palmitic, stearic, oleic, linoleic, and *iso*linolenic acids.

Trifolium repens.—The flowers of the white clover, *T. repens,* according to Perkin and Phipps (J.C.S. 1904, **85,** 58), owe their tinctorial property to quercetin which is present as glucoside.

Nakaoki (J. Pharm. Soc. Japan, 1933, **53,** 238) isolated *trifoliin* from the flowers and considered this to be a quercetin rhamnoside. According to Hattori, Hasegawa, and Hayashi (Acta Phytochim. 1937, **10,** 147), however, trifoliin is identical with *iso*quercitrin (quercetin 3-glucoside). A. G. P.and E. J. C.

CLOVES, ESSENTIAL OIL OF. Distilled from the unexpanded flower buds of *Eugenia caryophyllata* Thunb. (Fam. Myrtaceæ), a native of the Molucca Islands and cultivated in Zanzibar, Pemba, Amboyna, Penang, Madagascar, and in the Seychelles, Réunion, Ceylon, and Mauritius. The yield of oil from the buds is 16 to 19%. The ripe fruits (mother cloves) and the stems yield 4 to 7% of oil slightly inferior in quality. The leaf oil is also distilled in Mauritius.

Constituents.—The chief constituent is the phenol eugenol, of which 80 to 92% is present. Eugenyl acetate occurs to the extent of about 3%. Other constituents are furfural, methylfurfural, dimethyl furfural, methyl amyl ketone, methyl heptyl ketone, methyl benzoate, methyl amyl carbinol, methyl heptyl carbinol, methyl and benzyl benzoates, methyl salicylate, and the sesquiterpenes α- and β-caryophyllene.

Characters.—A colourless or pale yellow oil, darkening on keeping. Sp.gr. 1·047–1·065, opt. rot. at 20° 0° to −1·5°, n_D^{20} 1·528–1·540, phenol content 82 to 92%. Soluble in 2 volumes of 70% alcohol. The phenol content is determined by adsorption with cold 5% aqueous solution of potassium hydroxide as described in the " British Pharmacopœia." C.T.B.

CLUPEINE is the protamine of herring sperm. It contains 15 amino-acid residues and 14 peptide linkages and yields on hydrolysis arginine (10 mols), serine (2 mols), proline, alanine and valine (1 mol. each); mol.wt. 20Z1.

COAL TAR.—The dark brown to black, oily to viscous product of characteristic odour obtained as a by-product of the carbonisation of coal in gasworks retorts or in coke ovens (*see also* Tar).

Coal tar is a colloidal system, the disperse phase consisting of coarse to ultramicroscopic particles, the so-called " free carbon," as determined by the matter insoluble in aniline or pyridine, the continuous phase being the complex mixture of solid and liquid chemical compounds which form the tar oils. According to Nellensteyn, resin-like hydrocarbons adsorbed by the free carbon act as protective colloids to confer stability on the system. Upwards of 120 compounds have been identified in coal tars formed at high temperatures, *i.e.* over 900°C. In the following list those shown in CAPITALS are produced commercially, those for which commercial methods of isolation have been devised but not yet applied on a large scale are shown in **black-face type.** The compounds are given in the general order of their boiling-points, but in some cases the compound may be found in a higher fraction than that indicated by its boiling-point owing to the formation of double compounds.

Boiling-point below 200°C.

Hydrocarbons. — n-*Butylene* and *homologues,* n-*pentane* and *homologues,* **cyclopentadiene,** *di-* and *tetra-hydrobenzene,* BENZENE, TOLUENE, **ethylbenzene,** p-, m-, o-XYLENES, **styrene,** n- and *isopropylbenzene,* o-, m-, p-*ethyltoluenes,* **mesitylene, pseudocumene, dicyclopentadiene,** *hemellithene, hydrindene,* INDENE and *homologues, tetramethylbenzenes, durene.*

Oxygen-containing Compounds.—*Acetone,* CUMARONE and *methylcumarone,* PHENOL, o-CRESOL.

Nitrogen Compounds.—*Acetonitrile,* PYRIDINE and its METHYL *di-* and *trimethyl homologues, pyrrol, aniline,* **benzonitrile.**

Sulphur Compounds.—*Ethylmercaptan,* CARBON DISULPHIDE, *thiophen* and *mono-* and *dimethyl homologues* and *ethyl sulphides.*

Boiling-point above 200°C.

Hydrocarbons.—*Penta-* and *hexamethylbenzene,* **methylindene,** tetra- and hexa-*hydronaphthalene,* NAPHTHALENE, α- and β-**methylnaphthalenes,** *dimethylnaphthalenes, diphenyl* and its *methyl* and *dimethyl* derivatives, 4:5-*benzoindane,* ACENAPHTHENE, FLUORENE and its *methyl* derivatives, **phenanthrene,** *fluoranthrene,* ANTHRACENE and its *methyl* and *dimethyl* derivatives, *pyrene, naphthofluorenes, triphenylene, chrysene, truxene, perylene, liquid and solid paraffins.*

Oxygen-containing Compounds.—m- and p-CRESOL, *acetophenone,* m-5-XYLENOL and isomers, m- and p-*ethylphenols, dimethyl-cumarone,* symm. *methyl-ethyl phenol, durenol,* α- and *β-naphthols*, diphenylene oxide and its *methyl* derivative.

NITROGEN COMPOUNDS.—*Tetramethylpyridine, quinoline* and isoquinoline and their *methyl* derivatives, indole and its *methyl* derivatives, *a-* and *β-naphthonitriles*, acridine and its *methyl* and *dimethyl* derivatives, *phenanthridine*, *a-* and *β-naphthylamine*, CARBAZOLE and its 2- and 3-*methyl* derivatives, *phenylnaphthyl carbazole*.

SULPHUR COMPOUNDS.—*Thionaphthen tetramethylthiophen, diphenylene sulphide, thiophenols*.

The properties and composition of coal tars are materially influenced by the type of coal carbonised, by the maximum temperature to which the tar vapours are exposed in the retort, and by the time of exposure to this temperature. The primary tar formed in the retort consists mainly of paraffin hydrocarbons, olefines, naphthenes, and phenols, and the wide variety of conditions governing secondary decomposition accounts for the range of composition of the products of high temperature carbonisation. The coal components are subjected to different degrees of heat and the secondary reactions overlap. In general, medium carbonising temperatures (900°–1,150°C.) and rapid removal of the tar vapours from the retort give a higher yield of tar (12–14 gallons per ton of coal) rich in paraffinoid hydrocarbons and in high-boiling phenols. The aromatic compounds present are in part highly hydrogenated and methyl-substituted, while the tar contains a high proportion of oils and a low proportion of pitchy matter and of material insoluble in pyridine. Such tars are obtained from vertical retorts, particularly if steaming is employed during carbonisation. In horizontal retort practice higher temperatures are employed (1,150°–1,350°C.) and the time available for secondary decomposition is related to the density of filling the retort charge. The yield of tar is normally 9–11 gallons per ton of coal, the content of phenols, now mainly phenol and cresols, is decreased, the pitch yield, naphthalene content, and matter insoluble in pyridine are increased, and the hydrocarbons are almost wholly of the aromatic series and of a lower degree of substitution. Under comparative carbonising conditions, Midland and Yorkshire coals yield tar containing more light oil and less naphthalene and anthracene than Durham coals. In general, young coals have the higher oxygen content and give a higher tar yield. In coke oven practice (temperature 1,000°–1,250°C.) the degree of pyrogenic decomposition of the primary vapours varies with the type of oven and with the time cycle, but generally tar yields are lower at 8½ gallons per ton of coal, the tar being relatively viscous, highly aromatic in character, the naphthalene content being high and the phenols and pyridine-insoluble matter low. Whereas in a vertical retort the vapours proceed upwards and escape through cool inner channels in the coal, in a horizontal retort the vapours travel along the hot upper surface and are exposed to radiant heat. In a coke oven the large mass of wet coal cools the walls and the tar in part condenses in the centre of the coal mass and later, as carbonisation proceeds, is again vaporised, the degree of further decomposition depending on the temperature of the oven top. Pyridine-insoluble matter (elementary analysis—C about 90%, H about 3%, balance O+N+S+ash) is the final product of decomposition of the tar vapours. Unless local heating occurs, the absolute amount of this matter does not increase during the subsequent distillation of the tar. The percentage of matter insoluble in toluene but soluble in pyridine is relatively constant in crude tars, but increases in amount during the tar distillation process, the formation ratio depending on the prior thermal history of the tar, and on the maximum temperature employed during distillation and period of exposure thereto (*see* Adam and Sach, J.S.C.I. 1929, **48**, 337T).

Typical properties of crude coal tars are:

	Horizontal retorts.	Vertical retorts.	Coke ovens.
Specific gravity at 15·5°C.	1·16–1·23	1·07–1·12	1·12–1·18
Distillation per cent. by wt. of dry tar:			
Light oil to 170°C.	3–4	3–6	1–3
Middle oil to 230°C.	7–12	11–16	5–10
Creosote oil to 270°C.	10–15	11–20	8–15
Anthracene oil to 350°C. (approx.) . . .	11–14	10–16	15–24
Pitch (medium grade)	58–67	45–54	47–65
Matter insoluble in toluene	12–23	3–8	5–15
Phenols by per cent. volume on dry tar . .	3–6	6–10	3–7

The pitch from a horizontal retort tar will contain 22–35% matter insoluble in toluene (free carbon) and will yield 53–70% volatile matter, that from vertical retort tar will contain 10–20% free carbon and yield 67–75% volatile matter. Coke-oven pitch gives on analysis 15–25% matter insoluble in toluene and 63–72% volatile matter.

Weiss and Downs (Ind. Eng. Chem. 1923, **15**, 1022) give results of a full investigation of the constituents of a coke-oven tar.

The calorific value of crude tar is gross 16,500–17,000, net 15,900–16,400 B.Th.U. per lb. The specific heat is 0·35±0·05 at 40°C., 0·45±0·05 at 200°C. ("International Critical Tables"). Spiers (Technical Data on Fuel, 1935) quotes as a typical ultimate analysis, C 86·0%, H 6·2%, N 1·8%, S 1·0%, O, ash, and errors 5·0%. The carbon-hydrogen ratios of low temperature, vertical, coke-oven and horizontal tars are respectively as follows: 85·6, 11·4; 88·0, 6·8; 89·0, 5·5; 91·5, 5·2.

When tar is distilled in an Engler flask, the specific gravities at 15·5°C. of the fractions are shown in the following table:

Fraction.	Horizontal tar.	Vertical tar.	Coke-oven tar.
230°–270°	1·03–1·04	0·990–1·00	1·035–1·05
270°–300°	1·05–1·065	1·00–1·03	1·06–1·07
300°–350°	1·095–1·11	1·05–1·075	1·095–1·11

The yield of fine products per ton of crude tar varies within wide limits, and the following figures are to be taken only as a general guide: 90's benzole, 1–2½ gallons; 90's toluole, ½–1¼ gallons; 90/160 solvent naphtha, 1½–2½ gallons; phenol, 8–15 lb.; cresylic acid, 20–35 lb.; 90/140 pyridine bases, 0·15–0·4 gallon; naphthalene, 20–100 lb.; crude anthracene, 3 to 15 lb.

Distillation.—The crude tar vapours from the retort after condensation are separated from the ammoniacal liquor fraction, and if agitation be avoided during subsequent cooling, the tar as finally separated contains 3–5% liquor by volume. The corrosion of tar stills is attributed to the ammonium chloride present in crude tar acting in conjunction with the resinols, *i.e.* compounds soluble in aqueous caustic soda, but which can be precipitated from solution in an organic solvent such as benzene by the addition of light petroleum. The heavier corrosive action of vertical retort tars has been found to be due to their higher resinol content (D.S.I.R. Report, 1935/1936).

Chemical changes, generally described as cracking and polymerisation, occur during distillation, and the greater these changes the lower the yield of oils distilling below 350°C. and the higher the yield of residual pitch. The extent of the reaction is a function of time and temperature, increasing in some geometric ratio with increase of temperature, and in an approximately arithmetic ratio with increasing time at a constant temperature. Above 345° permanent gases and water are evolved; between 300° and 345° the decomposition is traced mainly by an increase in the pyridine insoluble matter and toluene insoluble matter (Weiss, Chem. and Ind. 1932, **10**, 219; Adam and Sach, *l.c*). Tars which have been subjected to high temperatures during formation are less susceptible to cracking during distillation. These factors, safety and fuel, labour and plant maintenance costs, must be considered in the design of efficient tar distillation equipment.

Crude coal tar, which may be preheated by indirect exhaust steam, is normally distilled in direct-heated wrought iron or mild steel vertical pot stills of 10–40 tons capacity, of height slightly greater than diameter, and having a concave bottom. The flues cause the combustion gases finally to encircle the walls of the still. Crude tar tends to froth over if rapidly heated, particularly if the insoluble matter content is high; to overcome this trouble, and at the same time to effect an economy in fuel consumption, modern pot still installations are now usually operated on the "double still" system, in which the vapours from the fire-heated still pass through a coil immersed in the crude tar for the next charge. The tar is thus sufficiently preheated to remove the water and naphtha fraction slowly, provided the water content is not higher than 7%. The general arrangement of the plant is shown in Fig. 1. Foul gases containing H_2S are evolved during distillation and are drawn off through an oxide bed or passed through an explosion prevention box to a furnace and burnt. Cracking during the later stages of distillation is reduced by the admission of dry free steam to the still, and the repeated circulation of inert gases such as CO_2 or nitrogen has been proposed to serve a similar purpose, thus increasing oil yields and reducing formation of insoluble matter in the tar (B.P. 158852). In America horizontal stills have been preferred. The satisfactory operation of the intermittent pot still depends very largely upon the skill of the man in charge, and the recent tendency has been towards the development of continuous units, which lend themselves to regularity of operation and control of distillate yields, to lower labour costs, to fuel economy by heat interchange between vapours and crude tar, and to relatively higher output per unit of capital expenditure. For example, a number of pot stills, say five, may be connected in series, and the tar progressively heated during its

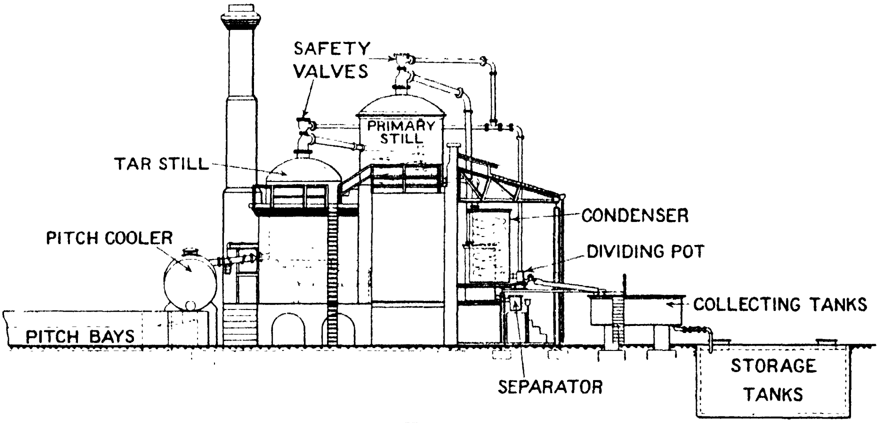


Fig. 1.

passage through the plant so that each still yields a selected distillate fraction. The Hird continuous plant (B.P. 11143, 1911) consists of a number of cast-iron stills in series, the heating gases passing through W.I. longitudinal tubes immersed in the tar. This type of plant, frequently combined with a steam-heated Wikner dehydrator (B.P. 191295) has been installed in a number of tar distilleries. In the Ab-Der-Halden system (B.P. 340370), largely employed in France, the tar, preheated by the outgoing pitch and by the flue gases is fed to a still into which superheated free steam is admitted. The hot gases from the coke furnace pass first over the steam superheating coil, then round the still, and finally over preheating coils. This plant is stated to give a high oil yield, and relatively good fractionation, but the steam consumption at 40–50% by weight on the tar is high. Kahl (B.P. 208691, 221773) superimposes a fractionating column on the still and thereby obtains a sharp separation of the fractions without re-distillation, thus facilitating the production of phenols, acenaphthene, fluorene, carbazole, etc. Owing to the lengthy exposure of the tar in the still to high temperatures, cracking and polymerisation occur and oil yields are low and pitch yields high.

Intermittent and continuous vacuum distillation has also been practised (Raschig, G.P. 260060; Weise, Petroleum, 1930, **26**, 499, 577). The T.I.C. process (B.P. 170617, 184624) takes advantage of the rapid transfer of heat that can be secured by feeding crude tar over the surface of a cushion of molten lead or alloy contained in a still—the distillation rate is high, giving high oil yields—and the fractional condensers give narrow range oil fractions. This system is used in gasworks with small daily throughput of tar.

In the Barrett (U.S.A.) system, tar is distilled by being brought into intimate contact with the hot coke oven gases by means of a rotating roller in a continuous still of special design (B.P. 346753, 347240, 349088, 370387), and the hard pitch produced, which may have a cube-in-air melting-point up to 400°F., is continuously removed and granulated by spraying with water. The hot gases and vapours from the still pass through heat exchangers and are then fractionally condensed. Suspended particles of tar in the vapours may be removed by means of an electrostatic precipitator before the vapours are passed to the condensing system. A small number of ovens on a battery are equipped to deal with the total production. It was claimed that the process gave maximum oil and minimum hard pitch yield with low operating costs, hence its development in the U.S.A., where, apart from the tar required for road purposes, the main objective of complete distillation is the production of creosote, pitch being a low value by-product. The throughput of the still varies with the oven cycle time and lies within the limits 100–125 gallons tar distilled per ton of coal carbonised. Cooke and Holton (B.P. 301645, 416103) use the sensible heat of the hot crude retort gases by circulating the tar in the collecting mains until a dehydrated tar of the required viscosity for road work is obtained; the light vapours pass forward with the gas and are recovered in a static extractor and dynamic extractor in series.

The pioneer user of the pipe or coil still was Lennard (B.P. 814 of 1891). His system improved in detail is employed by the South Metropolitan Gas Co. The preheated crude tar is pumped through a pipe still and at a temperature of 325°C. enters the top of a column into the base of which steam is admitted. Pitch is continuously drawn off from the base of the column and the vapours pass forward through a series of fractional condensers maintained at progressively lower temperatures. In 1907 Wilton (B.P. 26910, 1907) erected a cast-iron pipe still, in which the tar was heated to 170°C., while being maintained under a pressure of 40 lb. per sq. in. The hot tar at the coil exit passed through a control valve to a flash chamber at atmospheric pressure, in which the tar layer was kept at 4–6 in. depth. The water and light oils flashed off without frothing and the dehydrated tar was further treated in pot stills. This system was developed to deal with tars of high water and insoluble matter content. It was later adapted for the production of road tars, the dehydrated tar from the first coil being passed through a second coil at temperatures up to 275°C. and at pressures up to 60 lb. per sq. in. This type of plant is employed by the Gas Light & Coke Co. at their Beckton works.

The pipe still system of distillation has certain advantages, including relative safety due to the small quantity of tar in the unit at any particular moment, and production of high oil yields due to the short time of exposure of the tar to the higher distillation temperatures. The system operates continuously, and since 1933 has been further developed by improved design of the heat exchangers and fractionating columns. The rate of flow of the tar in the pipe still is such as to give turbulent flow conditions, thus minimising the formation of deposits in the pipes and increasing the rate of heat transfer. The heating surface has been designed to give a uniform rate of heat transfer per unit of surface and finally, bubbling hood towers with controlled reflux ratios have been added to yield narrow range fractions of oil.

Wilton (B.P. 307577, 337581, 424645) circulates the preheated tar through a pipe still to a vapour box and part of the residual pitch is passed again to the feed tank, where crude tar is admitted so that the hot pitch effects dehydration of the tar and distillation of the most volatile constituents. The mixture is again circulated through the still, the temperature being raised to 300°C. or higher.

In the American pipe still system the tar is dehydrated in the heat exchanger system and distilled by one passage through the still. Plant of this type in U.S.A. vary in capacity from 150 to 450–700 tons per day. Oil yields are 10–15% higher than for batch stills when producing pitch of cube-in-air melting-point 300°F. Final temperatures are higher than in pot stills, but the time factor is reduced to below $\frac{1}{15}$.

Adam and Potter (B.P. 303038) patented a two-stage pipe still distillation system designed to give a minimum increase of toluene-insoluble matter and hence high oil yields. Two coils set in one furnace operate under pressure and in series, the pressure being released in a flash box at the exit of each coil. The release of vapours in the second box is assisted by the admission of superheated free steam and the vapours are fractionally condensed in a series of bubble hood columns.

The Koppers Co. have erected a plant at Ostrava, Czechoslovakia, and another at Beckton, England, designed on similar principles. The tar is distilled in two stages, in two separate pipe stills between which is inserted a vaporiser for the removal of light oils and water. The tar is heated in the first still to 150°, and in the second to 300°–350°, according to the hardness of pitch required. The volatile products from the pitch column are carried forward and separated into the required fractions in successive bubble hood column stills with the aid of free steam. The first named plant has a capacity of 200 tons and the second 400 tons a day, the fractions taken comprising light oil, carbolic oil, crude naphthalene, wash oil, and two anthracene oil fractions—*see* Fig. 2. This system is economical only when a large tonnage is to be handled (100 tons per day or over). The heat units fed to the furnace per ton of tar distilled are 980,000 B.Th.U. in the form of solid fuel, and 96,000 B.Th.U. as steam (from pump exhausts), a reduction of over 25% on average figures for pot stills (Eisler, Zamrzla and Weinkopf, Glückauf, 1936, **72**, 184), which are of the order of 130–145 lb. coal per ton of tar distilled.

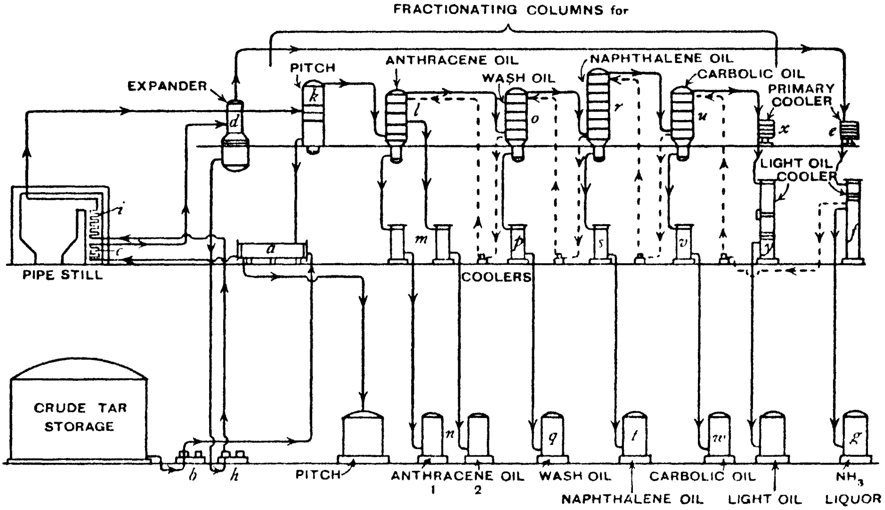


Fig. 2.

In another type of plant the hot tar is flashed into a tall bubble hood tower which embodies the evaporator or flash box section and the vapour rises through the trays on which it contacts with descending reflux liquid. At selected points on the tower distillate side-streams are drawn off.

The composition of the fractions obtained by primary distillation of crude tar varies considerably with the type of plant and type of crude tar. The following data are typical for a modern pipe still (Koppers) and for a double pot still installation distilling a mixed crude tar.

Pipe Still with Fractionating Columns.—The crude naphtha distils 95% between 90° and 170°C., sp.gr. 0·885–0·890, yield about 2–3% ; the carbolic oil distils 95% between 180° and 210°, sp.gr. 0·98–1·00, yield 3–6%, content of phenols 30–40%, this fraction being fluid at ordinary temperatures ; the naphthalene fraction distils 95% between 211° and 237°, crystallising point about 65°C., yield 6–10% ; the wash oil distils 95% between 240° and 290°, sp.gr. 1·025–1·040, yield 6½%, this fraction also being fluid at ordinary temperatures ; the anthracene oil No. 2 distils 95% between 263° and 330°, sp.gr. 1·07–1·08, yield 5% ; the anthracene oil No. 1 commences to distil at 323° sp.gr. 1·10–1·12 yield 15–20%.

Pot Still.—Crude naphtha, sp.gr. 0·910–0·960, distils 50–80% within the range 90°–160°, contains 60–65% benzole hydrocarbons, up to 15% naphthalene, and 5–10% phenols, yield 2–4%. The middle or carbolic oil, sp.gr. 0·960–1·005, distils mainly between 165° and 245°, contains up to 40% naphthalene depending on the nature of the tar distilled, and 15–30% phenols, yield 6–14%. The creosote oil fraction, sp.gr. 1·025–1·045, distils mainly between 220° and 300°C. Under favourable market conditions the phenols may be recovered by a caustic soda wash, otherwise this oil is mixed without chemical treatment with the anthracene oil fraction to yield timber preserving oils to the British Standard Specifications (*see* Creosote). The anthracene oil fraction, sp.gr. 1·075–1·11, distils mainly between 270° and 350°, yield 10–20%. In order to preserve the life of the still and to reduce decomposition, this fraction is obtained with the aid of free steam. After condensation of the vapours, the water is separated and the oil may be cooled to deposit crude anthracene of about 35% strength. The crude anthracene is recrystallised from solvents such as pyridine and solvent naphtha to yield a high grade anthracene and crude carbazole.

The distillation is carried to the point at which the pitch residue in the still has the desired softening-point when examined by one of the standard methods, the end point being determined by the specific gravity or by the appearance of the final runnings or by the temperature of the pitch or vapours. Normally there are three main halts: (1) the soft pitch stage (Kraemer-Sarnow softening-point, 25°–50°C.), the product being employed for various industrial purposes such as hot process tar-macadam and pipe coating for prevention of soil corrosion. The pitch at this stage is allowed to cool off to some degree in the still and is then run to containers or to the mixing plant ; the soft pitch may be cut back with a selected creosote oil fraction to yield road tars of the required viscosity; (2) the medium soft or briquetting pitch stage. This pitch has a softening-point 70°C.±5° by the Kraemer-Sarnow method, or 78°C.±5° by the Ring and Ball method. This grade is run from the still to coolers which may be storage vessels with an exit to air through a packed tower down which heavy oil is allowed to trickle for condensation of the heavy obnoxious vapours. From the coolers it is pumped while still fluid, either by steam-heated reciprocating pumps or by air pressure, the dry air being admitted through the molten pitch, to overhead cooling trays of 5 tons capacity, or alternatively, it is run by gravity to wrought iron moulds holding 1–2½ cwt., or to pitch beds, where it is allowed to cool to atmospheric temperature. The beds are concrete or brick-lined, and adhesion of the pitch is prevented by lime-washing the sides and covering the bottom with a shallow layer of coal dust; (3) the hard pitch stage, the product having a Kraemer-Sarnow softening-point 100°C. and upwards. This pitch is cast in cooling trays and is used for special industrial purposes, such as clay pigeon manufacture, as a reducing agent in metallurgical processes, as a fuel, or it may be further distilled in special stills or in coke ovens to produce pitch coke.

The naphtha, light oil, and carbolic or middle oil distillates are chemically treated to remove phenols and bases. Narrow range fractions are then prepared by redistillation for further resolution into the pure compounds.

The fraction to 170° is washed with 10% caustic soda solution to remove phenols, which are recovered as such (*see* Carbolic Acid), and with 25–30% sulphuric acid, crude pyridine bases being recovered from the acid solution by neutralisation with gaseous ammonia or sodium carbonate. The neutral fraction is then redistilled from a still fitted with closed steam coils, crude benzole, toluole, and solvent naphtha fractions being taken. These fractions are refined by treatment with 3–4% by volume of strong sulphuric acid (C.O.V.) to remove thiophen, and olefinic hydrocarbons, neutralised by water and alkali washes, and fractionally redistilled to yield pure and 90's benzole, pure and 90's toluole, xylole, and solvent naphtha. Until 1930 benzole for use as motor spirit was refined by similar methods. It was then recognised that the sulphuric acid gave rise to unnecessary losses of the order of 5–10%, due to sulphonation of the aromatic hydrocarbons and to the removal of the olefinic hydrocarbons which have a definite fuel value. In Germany a restricted acid wash employing 80% sulphuric acid was adopted, the treated spirit being distilled through a 60% caustic soda solution to remove sulphonic acid esters. In this country the inhibitor process was adopted, in which the chemical treatment is reduced to that necessary for removal of phenols and bases and for reduction of the sulphur content, and to improve the colour keeping properties. The formation of gum from the unsaturated hydrocarbons during storage is prevented by the addition after redistillation of small amounts of the order of 0·02% of substances known as inhibitors. Suitable inhibitors for benzole are cresylic acid of high ortho- content or catechol (Hoffert and Claxton, J.S.C.I. 1930, **52**, 25T).

The carbolic or middle oil fraction may be separated into two main fractions by redistillation and the lower boiling fraction washed for recovery of phenols, or the whole fraction may be so treated (*see* Carbolic Acid; Cresylic Acid). The first and second fractions obtained on redistillation, or the whole fraction, is cooled in pans or in tanks fitted with agitators and the crude naphthalene which crystallises out is separated by draining or centrifuging, and may be further purified by hot pressing. The crude naphthalene so obtained is washed in the molten condition with 4% sulphuric acid 93–96% strength, with hot water and with caustic soda solution, and redistilled or sublimed to yield the commercially pure product. The treated carbolic oil is redistilled, the fraction distilling between 160° and 190°C. being sold as "heavy naphtha."

The separation of tar into an oil fraction and a pitch fraction by treatment with light petroleum, b.p. 40°–60°C., and determination of the phenols and neutral oils in the soluble portion and of *resinoids* soluble in benzene but insoluble in light petroleum, forms the basis of a useful method for the examination of crude tars. Industrial applications of this method have been patented by Lessing (B.P. 130362) and Morgan and Pratt (B.P. 307566, 331542), but have not been developed on a large scale for the treatment of high temperature tars.

Commercial Evaluation.—The production of tar from coal was first mentioned by Becher in 1665 and later covered by a joint patent with Steele (B.P. 214 of 1681). Clayton (1739) carbonised coal with recovery of by-products, the tar being used in place of Stockholm tar. From the beginning of the nineteenth century until 1850 coal tar was in the main regarded as a useless by-product of the new illuminating gas industry. Early uses were as fuel for retorts, in the manufacture of roofing felt, as a paint for wood and stone, and for production of lamp blacks. The distillation of tar is first recorded in 1822, and in 1830 Anderson at his works in Edinburgh was producing naphtha which was sent to Macintosh in Glasgow for employment as a rubber solvent. His works also produced pitch and carbon black. The first important bulk outlet was opened up in 1838 when Bethell patented the employment of coal tar creosote oil for the preservative treatment of timber for railway sleepers and mine props—this use arose from the rapid decay of the sleepers on the Stockton–Darlington railway, opened in 1825. The light solvents were used as such and as illuminants. Following Hofmann's identification of benzene in coal tar (1845), Mansfield in 1848 laid the foundations of the industrial process for the recovery of benzene from coal tar. From 1856 onwards the development of the aniline dye industry, employing as raw materials benzene, toluene, naphthalene, and anthracene (alizarine 1868), exerted a strong influence. The employment of pitch for coal briquetting in 1842 extended the uses to which the products of primary distillation were applied. The production of tarred roofing felt increased, later to decrease in this country, but was maintained in U.S.A. and Germany. From about 1910 a new factor of immense importance arose with the development of the use of refined tar in road construction, both for surface dressing and for the manufacture of tarmacadam. Topped tars were first used on roads to eliminate the dust nuisance which followed the introduction of the motor car (1896), but later prepared tars were produced which, acting as a binder for the mineral aggregate, gave a road surface possessing the required qualities of stability, durability, and safe riding surface.

The production of crude tar increased in this country and more rapidly on the Continent with the introduction of the by-product oven for the manufacture of metallurgical coke (1876 onwards). A further important step was the introduction in Germany in 1890 of the gas washing process for the recovery of benzole from the coke oven gases, this materially reducing the export of benzene from England to the German dye manufacturers.

The quantity of crude tar produced by the gas industry has tended to increase, but the production from coke ovens undergoes marked changes in accordance with the state of the steel industry. Total production, therefore, bears no relation to the demand for the products of distillation, the values for which undergo relatively violent changes as the demand of the respective using industries equals or falls below the supply. The post war employment of the benzole hydrocarbons as motor fuels conferred on these constituents a relatively stable price in an unsaturated market. The market values for naphthalene, phenols, and cresols have not been without interest, but the real economic factor for the tar distiller is the price realised for the bulk products, creosote, pitch, and road tar. Data regarding the production of these products is given in the appropriate articles. Thus the value of tar as a by-product depends upon many factors, including the cost of transport of crude tar to the distillery, and of the products to the consumer. Present average values in the gas industry are 2½*d.* to 3*d.* per gallon crude tar, equivalent to 2*s.* to 3*s.* 3*d.* per ton of coal carbonised.

On the continent of Europe tar distillation practice follows the same general lines as British practice. In the United States the outlet for pitch is limited and hence about one-half of the crude tar produced, after removal of the more valuable light oils, is burnt as fuel in the adjoining steel works. At the tar distillation works, hard pitch for fuel purposes is produced, in order that the maximum yield of creosote oil may be obtained. As illustrating recent American conditions, the following figures supplied by S. R. Church are interesting: "The revenue per American gallon of coke oven tar fell steadily from 5·1 cents in 1929 to 3·7 cents in 1933, and had recovered to 4·1 cents in 1935."

Complete production statistics for Great Britain are not readily available, but the following data for 1936 has been assembled from the Annual Reports of the Chief Inspector of Alkali, etc., Works, England and Wales, and from other sources:

Origin of Tar.	Tar distilled.	Pitch produced.	Pitch exported.	Tar treated for production of road tar.	Road tar exported.
	tons.	tons.	tons.	%	tons.
Gas works	1,060,000	275,200			
Coke ovens	709,900	260,500			
Other works . . .	20,000	7,600			
Total	1,789,900	543,300	407,459	43	169,984

The figures for Scotland are: Tar distilled, 173,046 tons; pitch produced, 47,707 tons.

The production in Germany for 1935 was 1,435,000 tons, of which approximately four-fifths was from coke ovens; the road tar consumption was about 159,000 tons. In 1936 the production rose to 1,680,000 tons. The French production of crude tar, approximately one-half from coke ovens, was 525,000 tons; 305,000 tons of tar were used for road purposes in addition to 171,000 tons of road tar imported. The annual production of tar in the United States from horizontal and vertical retorts is about 220,000 tons, and from coke ovens, including those on gasworks, was 2,017,500 tons in 1935 and 2,588,000 tons in 1936; in 1935, 465,000 tons were used for road purposes. The quantity of tar distilled in the United States has increased in recent years—the figure for coke oven tar in 1932 being 811,500 tons and in 1935 1,316,000 tons, the balance of production in each year being either burned as fuel in steel works or sold as fuel.

The total world production of crude tar is of the order of 7–8 million tons.

Analysis.—Standard methods for testing tar and its products are fully described in the book issued by the Standardisation of Tar Products Tests Committee (2nd ed., 1938), which should be consulted. Methods for sampling are given in this publication and in British Standard Specification 616/1938.

The following determinations are normally made on a sample of crude tar: Specific gravity, water (by distillation), matter insoluble in toluene, ash, and distillation test, followed by the estimation of phenols and of crystallisable solids in the fractions. For the distillation test, the flask containing about 250 c.c. tar is heated in a fusible alloy bath and fractions to 210°, 230°, 270°, 300°, and 360°C. are collected, and the phenols, taken as the volumetric percentage of the fractions recorded. Alternatively, distillation may be conducted in a tared steel still, about 5 litres of the sample being taken, fractions being collected as before. Pyridine bases and phenols are extracted from the oils distilling to 270°, the former by 25% sulphuric acid, and the latter by 10% aqueous caustic soda solution, both being volumetrically determined by neutralising the respective solutions. The oil fractions to 270° are cooled to 15·5°C. and the naphthalene which separates is transferred to a Buchner funnel, pressed, and weighed. Similarly, the crude anthracene which separates from the oils distilling between 300° and the pitch point is determined. The pitch remaining in the still is weighed and the softening point, which should normally be 65°–75°C. by the Kraemer-Sarnow method, is determined. The washed light oils fractions are redistilled and the benzole (to 100°), toluole (to 120°), solvent naphtha (to 160°), and heavy naphtha (to 190°) fractions are measured (*see also* Pitch, Road Tar).

Literature.—A. R. Warnes, " Coal Tar Distillation," 3rd ed.; Lunge, " Coal Tar "; Rosendahl, " Steinkohlenteer "; J. M. Weiss, Chem. and Ind. 1932, **10**, 219, 246; E. Weise, Petroleum, 1930, **26**, 499, 577; " Standard Methods for Testing Tar and its Products " 1938; P. Spielmann, " The Constituents of Coal Tar "; Longmans, Green & Co., British Standard Specifications (various). F. M. P.

COBALT Sym. Co, at. wt. 58·94, at. no. 27. Isotopes 57, 59.

Occurrence.—Cobalt usually occurs combined with arsenic or sulphur, and is almost invariably associated with nickel and other metals. Metallic cobalt occurs in meteorites. The most plentiful and important ore of cobalt is *smaltite* or *tin white cobalt*, $CoAs_2$, which usually contains some nickel owing to the presence of *chloanthite*, $NiAs_2$, and also iron. Sulpharsenide of cobalt, $CoAsS$, occurs as *cobaltite* or *cobalt glance*. As hydrated arsenate, $Co_3As_2O_8,8H_2O$, the metal is found in *erythrite* or *cobalt bloom*, and as sulphide it occurs in *linnæite* or *cobalt pyrites*, Co_3S_4. *Asbolite*, *asbolan*, or *black earthy cobalt* is essentially *wad* (hydrated manganese oxide) containing a variable quantity of cobalt oxide mixed with it, sometimes amounting to 40%, sulphide of cobalt and oxides of copper, nickel and iron are frequently present. Cobalt occurs in small quantities in many other minerals—in pyrites and certain iron ores, in mispickel, in sulphide of lead, in cerite, and in some peats and coals.

The most important source of cobalt is Northern Rhodesia, where it occurs as cobaltiferous copper ore in the N'Kana mine of the Rhokana Corporation; next in importance comes the Belgian Congo, where it also occurs as cobaltiferous copper ore in the Katanga region, followed by the Cobalt district in Ontario, where smaltite and cobaltite are found abundantly in the silver ores, the cobalt minerals running in veins. In Sudbury, Ontario, cobalt occurs as cobaltiferous pyrrhotite associated with nickel, and is recovered as a by-product. Other sources are Burma, where nickel speiss carrying 3–4% cobalt is a by-product from the Burma Corporation smelting operations, French Morocco, where it occurs mainly as smaltite, and China, where it occurs as cobaltite and smaltite. Asbolite occurs in New Caledonia and also near Port Macquarie in New South Wales. Cobalt has also been obtained from Schneeberg in Saxony, Joachimsthal in Bohemia, Central India, Tunaberg in Sweden, Narimanov in Russia, and Cornwall.

Extraction.—The methods adopted for the extraction of cobalt from the ores vary with the nature of the ores, and as these generally contain larger quantities of some other metal than cobalt this latter is obtained as a by-product in the form of a speiss containing also arsenides of other metals, as a matte containing sulphides of other metals, or as a precipitate during wet treatment of ores.

Experiments on flotation concentration have given some interesting results. Starting with an ore containing 15·81% Co associated with pyrites and sphalerite, the Canadian Government Laboratories have succeeded in getting a 97% recovery of a 24·77% concentrate, and an 85% recovery of a 29·5% concentrate by flotation (J. S. Godard, Canada Dept. Mines, Mines Branch, Rep. 728, 1933, 75–76).

When cobalt ores are treated direct, they are smelted in low-pressure blast furnaces or cupolas together with fluxes which vary according to the nature of the minerals present. When silica is present in excess, lime is added, and when lime or alumina is in excess silica or a siliceous ore is added to the charge. If the slag obtained be too viscous, then fluorspar is also added. When arsenides are thus smelted a speiss or arsenide is formed, which is tapped from the furnace at certain intervals for subsequent treatment. The slag obtained may contain 1 to 2% cobalt, it is re-treated in the furnace by which means its cobalt content may be reduced to 0·5% or less. With sulphide ores, which are uncommon, a similar treatment results in the formation of a matte or sulphide containing the cobalt which also is subsequently treated for the separation of the cobalt.

During the smelting for speiss or matte, a certain amount of iron is allowed to go into the product because its presence reduces the amount of cobalt able to pass into the slag, and the iron is also useful in the subsequent separation of arsenic, and in the manufacture of ferro-cobalt.

The speiss as obtained is crushed, finely ground, and roasted in a mechanically rabbled furnace, the arsenious oxide which is driven off being condensed in long flues or in some form of dust precipitation chamber, collected and re-sublimed for sale as white arsenic of commerce. This roasting is continued until the roasted mass contains 10% arsenic, when it is removed from the furnace and again ground. The material is treated with hydrochloric acid and heated and agitated by means of live steam; the cobalt, nickel and copper oxides present are converted into chlorides, and the chlorine evolved oxidises the ferric arsenide to ferric arsenate, which, being soluble in hydrochloric acid, remains in solution. The solution is allowed to settle and is then filtered, any insoluble compounds including siliceous matter being left behind as a residue. The solution is nearly neutralised with milk of lime and the ferric arsenate is precipitated. Should there be insufficient iron present to convert all the arsenic into ferric arsenate, iron is added to the solution as ferric chloride. Any arsenic not precipitated by this method, together with any copper present, is precipitated by gassing with hydrogen sulphide; if the copper is high in quantity, it is separated electrolytically. Any iron not previously precipitated is removed by treating the solution with milk of lime until neutral to litmus and adding bleaching powder solution, then filtering off the ferric hydroxide. The solution thus obtained contains cobalt and nickel chlorides, together with traces of impurities, and is of a fine port-wine colour. It is treated with milk of lime and bleaching powder solution which precipitates the cobalt as hydrated oxide, $Co_2(OH)_6$. With care, this operation can be so adjusted as to stop at a point where the red colour of the solution just disappears, leaving a green colour characteristic of nickel chloride, thus:

$$2CoCl_2+CaOCl_2+2Ca(OH)_2+H_2O = Co_2(OH)_6+3CaCl_2$$

The green-coloured solution is treated with milk of lime, when the whole of the nickel is precipitated as green nickel hydroxide (T. H. Gant, Chem. and Ind. 1925, **44**, 157).

The black precipitate of cobalt hydroxide obtained as above is transferred to tubs, where it is boiled with dilute hydrochloric acid for the removal of traces of nickel. It is then filter-pressed and roasted, being finally wet-ground, again treated with dilute hydrochloric acid, washed to remove soluble lime salts and further traces of nickel, filter-pressed, and again roasted, when it is dehydrated and converted into the oxide, Co_2O_3, which is ready for the market as such or for reduction to the lower oxide or to metal.

When the product of the first smelting is a matte, as from sulphide ores (New Caledonia), this matte is carefully roasted at a moderate temperature only and the sulphides of the metals present, iron, copper and cobalt, thus oxidised to sulphates. These sulphates are dissolved in water and the iron present is precipitated by the addition of the requisite quantity of sodium carbonate. The copper and any heavy metals present are separated by hydrogen sulphide, which is filtered off. After boiling off the excess of hydrogen sulphide the cobalt is precipitated by the addition of sodium hypochlorite (bleaching-powder cannot be used owing to the presence of sulphates in the solution), and the nickel in the remaining solution is precipitated by sodium carbonate.

At La Panda (Belgian Congo) the cobaltiferous copper ores are first smelted for copper in a blast furnace and the slag, which contains about 6·5% Co, 5% Cu, and 10% Fe, is charged with a calcareous flux and a little coke into open single-phase electric furnaces taking 6,000–8,000 amp. The product is an alloy containing approximately 28% Co, 30% Cu, and 40% Fe, together with a slag which is returned to the copper smelting furnace. The upper electrode is of graphite and the lower electrode is embedded in the conducting hearth of the furnace. The furnace takes 50-cycle A.C. at 60 volts and consumes about 2,000 kw.-hr. and 8-9 kg. of electrodes per ton of alloy produced (R. Sevin, J. four élec. 1927, **36**, 17, 211). This alloy is exported to Belgium, where it is treated for the recovery of cobalt and copper. It is crushed and treated with sulphuric acid so that the cobalt and iron pass into solution and the copper remains as a metallic sponge. Iron is removed from the solution by the addition of lime and blowing in air, and after further purification the resulting cobalt sulphate solution is electrolysed (J. Leemans, Chim. et Ind. 1927, **17**, 87).

Until recent years the only market for cobalt compounds was in the ceramic industry, but the metal itself is now largely used for electroplating and as a constituent of many alloys. The cobalt sesquioxide, Co_2O_3, produced as above, when heated to a high temperature, yields the monoxide CoO. Metallic cobalt is produced by heating the oxide with carbon or carbonaceous material, starchy matter often being used; in this latter case the mixture is made into a paste, shaped, and cut into cubes which are heated to a high temperature in a retort. The metal so obtained is not melted down and contains a certain amount of free carbon. Cobalt is also produced as a grey metallic powder by heating the oxide in a current of hydrogen; if too low a temperature be used (250°) the resulting metal will be *pyrophoric*, igniting and becoming reoxidised in contact with air, the ignition temperature being 3° only. Carbon monoxide readily reduces cobalt oxide at temperatures above 500°, the reduction being very rapid at 900°. Reduction with aluminium by the thermit process gives a metal containing about 0·1% aluminium (Kalmus, J. Ind. Eng. Chem. 1914, **6**, 107). Pure cobalt may be obtained as a powder by heating cobalt oxalate, $Co(CO_2)_2$. A button of the pure metal may be obtained by fusing the oxalate alone or a mixture of the oxide and charcoal under a layer of suitable glass; the fusion is preferably performed in a lime or magnesia crucible at the highest temperature of the furnace. Pure cobalt may also be obtained by electro-deposition from a suitable electrolyte and by heating cobalt carbonyl.

PROPERTIES.—Cobalt is a brilliant silver-white metal with a slight bluish tinge. It ranks next to iron as a magnetic metal and retains its magnetism at high temperatures; above 1,100°–1,150°, however, it becomes para-magnetic. There are two allotropic modifications of cobalt: α-cobalt exists at ordinary temperatures and has a stable, close-packed, hexagonal lattice, but at 400° β-cobalt is formed, which is stable above this temperature and possesses a face-centred cubic lattice. Both varieties may exist side by side at ordinary temperatures, but α-cobalt is the stable form and β-cobalt the unstable form. Cobalt melts at 1,480° and boils at 2,375°/30 mm. Its specific gravity is 8·756 as cast, 8·81 after annealing, and 8·925 after swaging. It is harder and more tenacious than iron, its Brinell hardness number varying between 124 and 130, its tensile strength being about 34,400 lb. per sq. in. in the cast state, 36,980 lb. in the annealed condition, and 100,000 lb. after rolling, and its compressive strength as cast 122,000 lb. per sq. in., after annealing 117,200 lb. per sq. in. Electrodeposited cobalt is harder than the ordinary metal, its Brinell number being 270–311, according to conditions (McNaughton and Hothersall, J. Electrodep. Tech. Soc. 1930, **5**, 63). The electrical resistance is $6{\cdot}4\times10^{-6}$ ohm per cm.^{3} for pure metal, and $8{\cdot}96\times10^{-6}$ for 99·73% samples; the specific heat between 15° and 100° is 0·1053. The presence of from 0·06 to 0·3% carbon in the metal increases the tensile and compressive strength and the electrical resistance but has little effect on the hardness. Pure cobalt may be machined in a lathe as readily as pure iron or nickel, but it is somewhat brittle; cobalt containing a small quantity of carbon machines like mild steel, and whilst pure cast cobalt cannot be swaged without cracking, the metal containing carbon may be rolled or swaged down from the cast state provided these operations are carried out on the hot metal. It is soluble in hydrochloric and sulphuric acids with evolution of hydrogen, and rapidly soluble in nitric acid; it is not attacked by hot or cold alkali, but if used as an anode in the electrolysis of alkaline electrolytes it passes into solution as colloidal cobaltous oxide. Cobalt occludes from 60 to 150 times its own volume of hydrogen, the amount varying with the mechanical condition of the metal. When heated, the powdered metal combines with chlorine, bromine and iodine. It decomposes steam at a red heat and if finely divided ignites when heated in oxides of nitrogen, and in a current of ammonia gas at 470° forms a nitride, Co_4N_2, which decomposes at 600°. Compact cobalt does not oxidise in air at ordinary temperatures, but it becomes superficially oxidised at a red heat; sulphur unites with red hot cobalt to form sulphide. When finely-divided cobalt is heated to 150°–200° in carbon monoxide at 100 atm. pressure, orange-red crystals of cobalt carbonyl, $Co_2(CO)_8$, are formed which melt at 51°, are soluble in alcohol or ether but insoluble in water, and decompose above 52° yielding $Co(CO)_3$, which further decomposes at 100° (*v.* CARBONYLS). Cobalt may be deposited as a fine lustrous coating on metals by the electrolysis of a neutral solution of the double sulphate of cobalt and ammonium. Deposited on diatomite brick, cobalt is a good catalyst for the hydrogenation of ethylene, causing rapid reaction at −20° (Pease and Stewart, J. Amer. Chem. Soc. 1927, **49**, 2783).

DETECTION AND ESTIMATION.—*See* CHEMICAL ANALYSIS (Vol. II, pp. 553, 578, 580, 612, 656).

ALLOYS OF COBALT.

Copper.—Cobalt forms with copper a series of alloys containing no definite chemical compounds. Two series of solid solutions are formed containing respectively 0–10% and 95·5–100% copper, and alloys between these limits consist of conglomerates of the two sets of solid solutions, solidification being complete at 1,105°; in these alloys also the magnetic change is lowered to 1,050°; alloys containing 99% copper are magnetic (R. Sahmen, Z. anorg. Chem. 1908, **57**, 1). The Brinell hardness number of the series increases with additions of cobalt to copper from 28 for pure copper to 180 for the alloy containing 90% cobalt. Cobalt has a marked effect on the electrical properties of copper, the specific resistance increases rapidly up to 3·2% cobalt, at which figure the resistance reaches 9·45 microhms per cm.^{3} at 20°. The addition of 3 to 5% cobalt gives alloys with a minimum temperature coefficient of resistance of about 0·00077 and a maximum thermoelectric effect of 33 microvolts for 1° difference of temperature. Copper alloys containing 1–6% cobalt are remarkably ductile, malleable and tenacious.

Gold.—Molten gold and cobalt are miscible in all proportions, the freezing-point curve of the series having two branches meeting at a eutectic at 997° containing 90% gold. Solid solutions are formed containing 0–5·5% and 96·5–100% gold. All the alloys are magnetic, the magnetisability falling off with increasing percentages of gold, rapidly at first, then more slowly.

Zinc.—With zinc, cobalt forms a series of solid solutions containing 0·5 to 18·5% cobalt. The saturated solution contains 13·4% cobalt and a eutectic containing 0·5% cobalt solidifies at 413°. The compound $CoZn_4$ is formed at 18·46% cobalt with a melting-point of 873°.

Aluminium.—Cobalt and aluminium form a series of alloys of which the freezing-point curve has been determined by A. G. C. Gwyer (Z. anorg. Chem. 1908, **57**, 140). This curve shows a maximum at 1,628° and 68·5% cobalt corresponding to the compound $CoAl$ and two breaks at 1,165° with 38% and at 940° with 20% cobalt. There are two series of solid solutions containing respectively 68·5 to 90·5 and 90·5 to 100% cobalt. There is a minimum on the curve at 1,375° and 90·5% cobalt. The compound $CoAl$ on cooling reacts with the liquid mass in alloys containing less than 68·5% cobalt at 1,165° to form the compound Co_2Al_5, and again at 940° to form Co_3Al_{13}. A eutectic occurs at 654° containing about 1% cobalt. The solid solubility of cobalt in aluminium is less than 0·02%.

Tin.—Cobalt and tin are miscible in all proportions in the molten state and the freezing-point curve has been determined by K. Lewkonja (Z. anorg. Chem. 1908, **59**, 294). This curve shows that when solid, the maximum amount of cobalt soluble in tin is 3·5%. There is a first eutectic at 1,088° and 34% tin and the eutectic line extends from 3·5% to 48% tin, at which point Co_2Sn forms and freezes at 1,151°. There is a second compound $CoSn$, which forms at 950°; this compound undergoes a polymorphic change at 536°. A second eutectic freezes at 230° with less than 1% cobalt and occurs in all alloys between pure tin and the compound $CoSn$, containing 66% tin.

Chromium.—Cobalt and chromium are mutually soluble both in the liquid and in the solid state. At a temperature of 1,320° the liquidus curve shows a minimum at approximately 47% cobalt. Alloys containing 45–85% chromium undergo a reaction at 1,225°, at this temperature the homogeneous solid solution breaks down into two solid solutions. Alloys containing 0–45% chromium show a polygonal structure containing cobalt-rich cores, the chromium increasing from the centre to the outside. In alloys containing more than 55% chromium the chromium content of the grains decreases from the centre to the outside. At room temperatures the alloys containing up to 25% chromium are magnetisable and the temperature at which loss of magnetism occurs decreases rapidly with increasing chromium content, the addition of 10% lowers the transformation temperature from 1,056° for pure cobalt to 686°, 15% to 300°, whilst the addition of 25% lowers it to below room temperature.

Ternary Alloys.—Chromium alloys, together with the ternary alloys containing cobalt, chromium, and tungsten, or molybdenum or the quaternary alloys containing all four of these metals, constitute an important class which are known under the name *Stellite*, from the Latin *stella*, for a star, chosen because of the brilliant polish such alloys take, and retain when exposed to ordinary atmospheric conditions. The straight binary alloys of cobalt and chromium can be cast into bars or other forms and are almost file-hard. They are slightly malleable when cold and distinctly so when hot, and can be further hardened by heating to redness and quenching in water. An alloy containing 70% cobalt, 25% chromium, and 5% tungsten is a distinctly harder alloy which forges at a red heat and takes a good cutting edge; this alloy is suitable for cold working tools such as chisels and wood-working tools. Much harder alloys are obtained by increasing the tungsten to 20%, at which point they can only be forged to a limited extent; and by increasing the tungsten to 25%, giving an alloy containing cobalt 60%, chromium 15%, and tungsten 25%, a very hard alloy is obtained which cannot be forged but is cast into bars which are subsequently ground and used as cutting tools for steel and cast iron. Molybdenum produces much the same effect as tungsten and the addition of 10% makes an excellent lathe tool. An alloy containing cobalt 45%, chromium 15%, and molybdenum 40% is very hard, cuts glass, and will even scratch quartz. A common range for the composition of stellite is cobalt 45–50%, chromium 25–30%, tungsten 15–20%, and carbon 2·5–2·75%. For cutting tools this may be used as cast bars or as tips which are brazed to shanks and blades fitted into slots in milling and boring heads. It has also been used for giving hard tips to picks, for the hard-facing of dies, and for facing aeroplane tail skids and the steel rings of cement kilns. *Stelliting* is the operation of depositing a layer of the alloy on steel or cast-iron by means of the oxyacetylene torch, the atomic hydrogen torch, or the electric arc, to form a hard wear-resisting surface. A new electro-chemical method of cladding ferrous products with stellite is described by R. R. Rogers (Ind. Eng. Chem. 1935, **27**, 783). *Widia* is another cobalt alloy consisting of tungsten carbide containing about 6% cobalt. It is used for heavy-duty lathe work and the turning of glass and bakelite, and is probably the hardest known alloy.

Iron.—Cobalt is an important constituent in certain steels, especially magnet steels, and when the metal is destined for use in the steel industry it is generally obtained as a mixture of iron and cobalt known as ferro-cobalt. This is marketed in the form of cubes containing from 10–15% iron and 80–90% cobalt.

Nickel.—With nickel it forms a series of solutions both in the liquid and solid condition.

Cobalt.—Cobalt dissolves 3·9% carbon at 1,700°, and at the eutectic temperature 1,300° cobalt retains 0·82% carbon in solid solution. The eutectic is found to contain only metallic cobalt and graphite but no carbide.

ELECTROPLATING.—Cobalt is used for electroplating purposes owing to the pleasing colour and resistance to tarnish of the deposited metal. It has been considered that cobalt deposits are harder than nickel deposits, but D. J. Macnaughtan (J. Iron and Steel Inst. 1924, **109**, 410) has shown that under varying conditions the Brinell hardness of cobalt deposits may vary between 270 and 311, that of nickel deposits may vary between 180 and 420. A suitable bath contains 565 g. cobalt sulphate (crystal), 20 g. sodium chloride, and 30 g. boric acid per litre. A current density of 100–160 amps. per sq. ft. may be used and the plating may be carried out more rapidly than with nickel (Brass World, 1926, **22**, 303).

COBALT AS A CATALYST.—An account of the reactions of olefins in the presence of metals has been given by G. Egloff and C. I. Parrish (Chem. and Ind. 1937, **56**, 321) in which cobalt is included. A cobalt catalyst prepared by calcining the nitrate on pumice followed by hydrogen reduction was heated in a current of ethylene (Walker, J. Phys. Chem. 1927, **31**, 961), no liquids were found up to 545° while much carbon was deposited. At 400° there was 40·5% decomposition yielding mostly hydrogen and a small amount of ethane, while at 545° there was 97·4% decomposition into a gas containing principally hydrogen, a small amount of ethane, and 13·0% methane. Reduced cobalt has no effect upon ethylene at ordinary temperature, but above 360° the gas was decomposed into hydrogen, ethane, and carbon with small quantities of benzene and its homologues. It is less active than nickel but acts similarly (Sabatier and Senderens, Compt. rend. 1897, **124**, 616, 1358; 1900, **131**, 267; Ann. Chim. Phys. 1905, [viii], **4**, 436).

COMPOUNDS OF COBALT.

Oxides.—There are three well-defined oxides of cobalt, namely, cobaltous oxide, CoO, cobaltosic oxide, Co_3O_4, and cobaltic oxide, Co_2O_3. *Cobaltous oxide* is obtained when cobalt is burnt in oxygen or when oxygen is blown through the molten metal. It is also obtained by roasting the powdered metal in air, by heating cobaltous hydroxide below 350° in a current of hydrogen, or by heating the hydroxide or carbonate in air. It varies in colour from greenish-grey, red, brown, to black, according to method of preparation and size of grain. *Cobaltous hydroxide*, $Co(OH)_2$, is precipitated when potassium hydroxide is added to a solution of a cobaltous salt out of contact with air as a blue or rose-red precipitate, the blue is considered to be CoO,H_2O, and the rose $Co(OH)_2$, the latter gradually turns brown in contact with air forming cobaltic hydroxide $Co(OH)_3$. *Cobaltosic oxide* is formed superficially when metallic cobalt is heated in air or by heating cobaltic oxide or hydroxide in air; when the product is heated in hydrogen it is reduced first to cobaltous oxide and then to metal. *Cobaltic oxide* is formed when a concentrated solution of cobaltous chloride mixed with potassium chlorate is evaporated to dryness, heated to a temperature of about 250°, and then extracted with water. On heating to 265° it decomposes, leaving Co_3O_4, and at a high temperature yields CoO. Impure forms of hydrated cobaltic oxide are found in various minerals and the oxidation of cobaltous salts in acid or alkaline solutions yields these compounds, the composition of the hydrate depending on the concentration and temperature of the solution and the nature of the oxidising agent used. The preparation of a number of definite hydrates has been reported, including $3Co_2O_3,2H_2O$; Co_2O_3,H_2O; $2Co_2O_3,3H_2O$; $3Co_2O_3,5H_2O$; $Co_2O_3,2H_2O$; $Co_2O_3,3H_2O$.

Cobaltous oxide is used for the preparation of the salts of cobalt and also of smalt the glass obtained by heating the oxide with certain fluxes such as sand. It is also used by enamellers and porcelain manufacturers for the production of the finest blue glaze and colour on porcelain glass and other vitrifiable substances. The presence of $\frac{1}{20000}$ of oxide imparts a bluish tinge to clear glass. The presence of other oxides has an injurious effect on the colour produced by this substance; it is therefore necessary, for the more delicate work, to ensure its complete freedom from such impurities.

When heated with magnesia it produces a pink mass; with alumina, a fine blue (Thenard's blue), and with zinc oxide a green (Rinmann's green). Zaffre is obtained by heating a mixture of roasted cobalt ore with sand to a temperature below the melting-point. (*v. infra*, p. 219*c*).

Pigments containing Cobalt.—*Thenard's Blue, Cobalt Blue, Cobalt Ultramarine, King's Blue* or *Azure Blue.*—The composition of this pigment varies considerably according to the method of manufacture. The original Thenard's blue was prepared with phosphate or arsenate of cobalt and alumina, but now cobaltous oxide and alumina are practically always used. Using the original method, it may be prepared by precipitating a solution of a cobalt salt, usually the nitrate free from iron and nickel, with potassium or sodium phosphate or with sodium arsenate. The gelatinous violet precipitate is thoroughly washed and well mixed with 3–5 volumes of freshly precipitated, well-washed alumina precipitated from a solution of alum free from iron by the addition of sodium carbonate. The mixture is dried and calcined at a cherry-red heat in a well covered clay crucible. When the desired blue colour has developed the mass is ground in water and dried.

A similar product may be obtained by the simultaneous precipitation of the oxides of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate and alum; the mixed precipitate is washed and heated as above.

According to Hedvall (Arkiv. Kemi, Min., Geol. 1914, **5**, No. 16, 1), cobaltous oxide and alumina are preferably ignited in presence of potassium chloride as a flux. When the cobaltous oxide is in excess the resulting product can be obtained pure by treatment with water to remove the flux and with hydrochloric acid to remove the excess of cobalt oxide. At 1,100° the blue aluminate, CoO,Al_2O_3 is formed; at temperatures above 1,100° a green aluminate, $4CoO,3Al_2O_3$, is produced. Wagner and Vanino found that cobalt sulphate could be used instead of phosphate and that the alumina was most suitably introduced as ammonium alum. To 22 parts alum were added 2·5 to 5 parts cobalt sulphate and 0·3 parts magnesium or zinc sulphate; the mixture was melted in its water of crystallisation and constantly stirred until dry, after which it was heated to the required temperature (L. Vanino, Chem.-Ztg. 1911, **35**, 497).

The Thenard's blue colours include the range of blues known as " Matt " blues. These are prepared by heating cobalt oxide with ammonium alum or potash alum and alumina with the addition of varying quantities of zinc oxide. From 20–30% of zinc oxide helps to weld the colour to the body in the ceramic industry without destroying the blue (T. H. Gant, Chem. and Ind. 1925, **44**, 160).

Thenard's blue is of a fine ultramarine colour; the presence of excess cobalt imparts a somewhat greenish tinge. It has, however, the disadvantage of appearing violet by gaslight. It is one of the most permanent blue pigments, being unaltered by acids or alkalis, and is largely used as an oil and water colour, but works better as water colour. It is non-poisonous and has the advantage of miscibility with other pigments without alteration.

Cæruleum, cæline or bleu céleste, is a corresponding colour containing oxides of tin and cobalt and calcium sulphate or silica. It is prepared by heating together cobalt sulphate, tin oxide, and precipitated silica or chalk and its general composition may be oxide of tin 49·66, oxide of cobalt 18·66, calcium sulphate or silica 31·68. It may also be prepared by precipitating a solution of cobalt nitrate with sodium stannate and heating the precipitate as above. It is a fine light blue pigment of slightly greenish tinge, of greater density than Thenard's blue, and retains its colour in artificial light.

New Blue is a blue pigment of shade varying from a pale greenish-blue to a deep turquoise blue, largely used for enamels, it consists of aluminates of cobalt and chromium produced by the action of alum on carbonates and hydroxides of cobalt and chromium, and the subsequent firing of the resulting precipitate.

Cobalt Green, Rinmann's Green.—The constitution of this pigment corresponds with that of Thenard's blue with the substitution of zinc oxide for alumina. It has been shown to be an isomorphous mixture of cobalt zincate ($CoO{\cdot}ZnO$) with zinc oxide which cannot be chemically separated (J. A. Hedvall and T. Nilsson, Z. anorg. Chem. 1932, **205**, 425). It may be prepared by mixing a solution of pure cobalt sulphate (or nitrate) into a paste with zinc oxide and heating in a muffle furnace for 3 or 4 hours until the desired colour is obtained. Pigments of a more uniform nature are produced by the precipitation of a mixture of solutions of zinc and cobalt salts by means of sodium carbonate, phosphate, or arsenate, drying and heating the precipitate. The phosphate is said to give a purer and brighter green colour than the carbonate.

Rinmann's green is a fine permanent pigment; its colour varies through many shades, according to the proportion of zinc oxide present, the darker greens containing less of that substance. It is non-poisonous and unacted upon by dilute acids or alkalis, but is attacked by ammonia. It has also the advantage of not affecting, or being affected by, other pigments.

Turquoise Green is another permanent green pigment prepared by firing a mixture of cobalt oxide, alumina, and chromium oxide, or sometimes the following proportion of freshly precipitated substances are fired: $CoCO_3$ 20, Al_2O_3 40, Cr_2O_3 20.

Cobalt Bronze is an ammonium cobalt phosphate of a violet colour, with a bronze-like metallic lustre.

Cobalt Yellow, Fischer's salt, aureolin, Indian yellow, consists of potassium cobaltinitrite prepared by the addition of potassium nitrite to a solution of a cobalt salt acidified with acetic acid. Its composition varies with the proportions used and the strength of the solution. Erdmann and Sadtler found that when precipitated from a solution containing much acetic acid, it consists of $K_3Co(NO_2)_6$ with a variable amount of water. It is a bright yellow crystalline powder, very free from impurities, unacted upon by cold water or cold acids, and but slowly blackened by sulphuretted hydrogen. It forms a fine pigment for artistic purposes and when used for painting porcelain it produces on baking the usual blue colour, which is of great beauty.

Cobalt Brown is produced by calcining a mixture of ammonium, ferrous, and cobalt sulphates.

Cobalt Red is produced by heating a mixture of magnesia and cobalt oxide. Solid solutions are formed the colour of which varies with the proportions of the oxides from light to dark red (Hedvall, Z. anorg. Chem. 1914, **86**, 296).

Smalt, Bleu d'Azur, Bleu de Saxe.—This important substance consists essentially of a potassium silicate glass coloured with cobalt. In the preparation of smalt in Saxony, smaltinte is principally used. In Norway and Sweden the principal ore is cobaltite. The general process is the same for both ores. The selected ore is powdered, freed from the lighter earthy impurities by a process of washing or concentration and roasted in a reverberatory or muffle furnace. The arsenic and sulphur are expelled as oxides, the former being condensed in chambers. The roasting should be continued until only sufficient arsenic is left to combine with the less oxidisable metals, especially copper and nickel, while the greater part of the cobalt is converted into oxide. The product is known as zaffre or zaffler, which is sometimes considered as a crude oxide of cobalt and sometimes as a basic arsenate and is used for painting on porcelain. Towards the end of the process of roasting a small portion is occasionally tested and the process stopped when the finest tinted glass is produced. The material is then ready for fusion for " smalt."

The fluxes used consist of powdered quartz and potassium carbonate. They must be very pure, as the presence of lime or many other substances impairs the beauty of the colour. The proportions of the ingredients vary according to the richness of the ore and the colour required. The potassium carbonate used generally amounts to about one-third of the weight of the zaffre and quartz together. White arsenic is sometimes added to reduce any ferric salt and thus prevent the injurious effect of that substance on the smalt and otherwise to heighten the colour of the product. The exact amount of each substance is found by a test fusion and comparison with a smalt of the required colour.

The mixture is melted down in crucibles or pots made of very refractory clay, free from lime; these pots are strongly heated and the mass fuses in about 8 hours, it is frequently stirred to render it homogeneous and to break the crust which forms on the surface. The quartz and potash react with the formation of fusible potassium silicate, which dissolves the cobalt oxide forming the blue smalt, while the mixed arsenides of nickel, copper, and iron with the small quantity of cobalt arsenide which is always present fuse and form a brittle, metallic-looking *speiss* beneath the smalt. This usually contains about 3% cobalt and a considerable quantity of nickel and these are recovered. The mass is left at a high temperature for some time without stirring, to allow the speiss to settle, and the smalt is then ladled out into vessels of cold water. It is thus rendered granular, brittle, and easy to pulverise. The blue glass is next ground under water and the product passed through a series of depositing vats for sizing, the coarser portions being reground and the finest portions being remelted if necessary. The marketable portions are dried and sifted. The presence of oxides other than those of cobalt and potash, even in small quantities, exerts a powerful influence on the colour of the smalt. Baryta produces an indigo tinge; sodium, calcium and magnesium produce a reddish shade; iron, a blackish-green very prejudicial to the brighter coloured smalts; manganese, violet; nickel, violet, but less intense; copper, zinc, bismuth and antimony, dull shades.

The composition of smalt varies considerably; the silica is usually from 56–70%, potash 12–22%, cobalt oxide 6–16%; it frequently contains small quantities of alumina, ferrous oxide, and lime. Smalt is a very permanent blue pigment largely used for the production of blue colours with vitreous substances. It was formerly used for colouring starch, paper, etc., but for this and many other purposes it is now almost superseded by artificial ultramarine, which, however, is far less permanent.

Uses of Cobalt in the Ceramic Industry.—In the form of oxide, cobalt is largely used in the ceramic industry in three main ways: (1) As a body stain, (2) as a glaze stain, and (3) as an underglaze or on-glaze stain.

(1) As a body stain cobalt is used because the clays used for nearly all pottery bodies contain iron which gives a yellow tinge to the fired goods. The added cobalt counteracts this by producing a complementary blue coloration which neutralises the yellow and gives a pure white colour. For carrying out this process black oxide of cobalt is mixed with about 10% of china clay, thoroughly ground with water, and passed through a 200-mesh sieve. The product is added to the pottery body in the wet state in the proportion of about 1 lb. cobalt oxide to 1 ton of dry pottery body. The exact quantity necessary is determined by trial. Sometimes the cobalt is added as chloride. For colouring bodies various shades of blue, cobalt oxides in larger quantities are used. In combination with oxides of manganese, nickel, and chromium, all shades of blue and green may be obtained with cobalt oxide.

(2) As a glaze stain the use of cobalt is most widely known in pottery manufacture because of the rich blue colours possible. The characteristic royal blue colour is obtained by adding 5% cobalt oxide to a glaze of high lead content. The oxide may be introduced either in the raw state or after fusing with a soft frit in a crucible, running into water, and grinding with the necessary quantity of glaze. All shades of blue, blue green, celadon glazes, etc., may be made by mixing the cobalt oxide with the oxides of iron, chromium, manganese, copper, and nickel.

(3) For under glazes or on-glaze colour stains either smalt blue, which gives an intense violet-blue colour characteristic of cobalt silicate, or Thenard's blue, a rich turquoise blue characteristic of cobalt aluminate, may be used.

ENAMELS.—In the form of smalt cobalt is used for the colouring of blue enamels. The oxide is also used in small quantities in the production of white enamels, thus neutralising any yellow due to the presence of iron. By the addition of cobalt oxide to certain raw mixtures and waste enamels a beautiful *black enamel* is produced which when added to other black enamels intensifies the colour; the compounds such as silicate, aluminate, and phosphate are largely used, as they give a more uniform colouring than the oxide. Cobalt oxides up to 0·5% are also used in the preparation of ground enamels for enamelling iron vessels. These oxides are found to increase the adherence of the enamels (T. H. Gant, *l.c.*).

Sulphides.—*Cobaltous sulphide*, CoS, is formed when sulphur is projected on to red hot cobalt, its formation being attended by incandescence and fusion. The freezing-point curve of the system Co–S has been determined up to 33·5% sulphur by K. Friedrich (Metallurgie, 1908, **5**, 212) and indicates the formation of the compounds Co_4S_3, Co_6S_5, and CoS. The following sulphides have also been reported by various workers: Co_2S, Co_3S_4, Co_2S_3, CoS_2, and Co_2S_7.

Arsenides.—The compound $CoAs_3$ occurs in the mineral *skutterudite* in Norway, and $CoAs_2$ occurs in the important mineral *smaltite*. The freezing-point curve of the Co–As series has indicated the existence of the compounds Co_5As_2, Co_2As, Co_3As_2, and $CoAs$ (K. Friedrich, Metallurgie, 1908, **5**, 150). The compounds Co_3As_2, $CoAs$, and Co_2As_3 have been prepared by Ducelliez (Compt. rend. 1908, **147**, 424).

Antimonides.—The compounds $CoSb$ and $CoSb_2$ have been indicated during the examination of the Co–Sb series by Ducelliez (Compt. rend. 1908, **147**, 1048).

Nitrides.—The *nitride* Co_2N is described by Beilby and Henderson (J.C.S. 1901, **79**, 1251); the *nitride* Co_3N_2 by Vournasos, Compt. rend. 1919, **168**, 889; *cf.* Bergstrom, J. Amer. Chem. Soc. 1924, **46**, 2631). The *azide* $Co(N_3)_2$ is highly explosive (Wöhler & Martin, Ber. 1917, **50**, 586.)

Silicides.—When metallic cobalt is heated to 1,200°–1,300° in silicon tetrafluoride vapour, the compound Co_2Si is formed as grey metallic crystals. This same compound, together with $CoSi$ and $CoSi_2$, has been prepared in electric furnaces. Other silicides have been reported by Jenge (Z. anorg. Chem. 1921, **118**, 105).

CARBONYLS.—There are two carbonyls of cobalt, the tetracarbonyl, $Co_2(CO)_8$, and the tricarbonyl, $Co(CO)_3$. The tetracarbonyl is prepared as follows: cobalt oxalate is heated until completely converted into the oxide, which is then washed free from traces of chlorides which hinder the formation of the carbonyl, and dried at 120°. The oxide is placed in a suitable apparatus and reduced to cobalt by means of hydrogen at 300°, and a pressure of 5 atmospheres. After reduction is complete the hydrogen is displaced by carbon monoxide, the pressure being increased to from 40 to 250 atmospheres and the temperature reduced to 150°–250°, when varying quantities of carbonyl are collected in a tube attached to the outlet of the apparatus and immersed in a freezing mixture.

The tetracarbonyl forms orange-coloured crystals of sp.gr. 1·73 which melt at 51° and decompose above that temperature. It is insoluble in water but is soluble in most organic solvents and in nickel carbonyl. It is not attacked by aqueous acids, but concentrated acids and the halogens decompose it forming the corresponding salt, carbon monoxide, and hydrogen:

$$Co_2(CO)_8+2H_2SO_4=2CoSO_4+8CO+2H_2$$

In contact with air, a deep violet-coloured compound is formed which is most probably a hydrated basic carbonate. The crystals are best preserved in a sealed tube in an atmosphere of carbon monoxide. When the tetracarbonyl is heated to 60° one quarter of the carbon monoxide is evolved at a regularly decreasing rate, leaving cobalt tricarbonyl, no intermediate product being formed. When heated to 100°, one-quarter of the carbon monoxide is evolved almost instantaneously, the rest coming off very irregularly and comparatively slowly (Mond, Hirtz, and Cowap, J.C.S. 1910, **97**, 798).

Nitric oxide reacts with cobalt tetracarbonyl slowly at ordinary temperature, but instantaneously at 40°, partly decomposing it into tricarbonyl and carbon monoxide and partly converting it into the nitroso-tricarbonyl $Co(CO)_3NO$, which is a cherry-red mobile liquid (Mond and Wallis, J.C.S. 1922, **121**, 33).

Salts of Cobalt.—The soluble salts of cobalt are prepared by the solution of the oxide, carbonate or metal in the various acids. They are generally pink and deliquescent, forming pink solutions when dilute, but when dried or in concentrated solution they are blue. For this reason solutions of chloride or nitrate of cobalt are used as sympathetic inks, such writing being almost invisible until brought near a fire, when the letters appear blue. They gradually reabsorb moisture and against become invisible. This change in colour has also been used for preparing "floral hydrometers" by tinting artificial flowers which in damp weather remain pink but in dry weather turn violet or blue.

When ammonia is added to solutions of cobalt salts oxygen is absorbed, giving rise under various conditions to many complex series of salts containing ammonia and known as cobalt-ammine salts which have received much attention (*v.* COORDINATION COMPOUNDS).

Cobaltous fluoride, CoF_2, is prepared by heating the chloride with ammonium fluoride in a current of hydrogen fluoride, and forms rose-coloured prisms slightly soluble in water (Poulenc, Compt. rend. 1892, **114**, 1426). The hydrated fluoride, $CoF_2,2H_2O$, is prepared by dissolving the oxide or carbonate in hydrofluoric acid; on evaporation rose-red crystals of the above composition are deposited (Edminster and Cooper, J. Amer. Chem. Soc. 1920, **43**, 2419).

Cobaltic fluoride, CoF_3, has been prepared by O. Ruff (Z. angew. Chem. 1928, **41**, 739) and by O. Ruff and E. Ascher (Z. anorg. Chem. 1929, **183**, 193) by the action of fluorine on cobaltous chloride in a quartz tube at 150°. When heated to 250° in hydrogen it is reduced to cobaltous fluoride, the reaction being complete at a red heat.

Cobaltous chloride, $CoCl_2$, is obtained by warming powdered metallic cobalt in chlorine gas; it ignites, forming blue crystalline scales of the anhydrous salt which can be sublimed in a current of chlorine. It is also prepared by dissolving the oxide or carbonate in hydrochloric acid and evaporating the solution. According to the temperature at which it crystallises, it may contain 6, 4, or 2 molecules of water of crystallisation, the last at the higher temperatures. The commercial salt contains 6 molecules of water and is violet in colour.

Cobaltous bromide, $CoBr_2$, is formed as a green fused mass of the anhydrous salt when bromine vapour is passed over metallic cobalt at a red heat. This salt absorbs water from the atmosphere, yielding a dark red liquid owing to the formation of $CoBr_2,6H_2O$.

Cobaltous iodide, CoI_2, is produced in the anhydrous state by heating metallic cobalt in iodine vapour. It is also obtained with evolution of heat when finely-divided cobalt is warmed with iodine and water.

Cobaltous sulphate, $CoSO_4,7H_2O$, is prepared by the solution of the oxide or carbonate in dilute sulphuric acid. It crystallises in red crystals isomorphous with magnesium sulphate soluble in 24 parts of cold water. The following hydrates $CoSO_4,6H_2O$, $CoSO_4,4H_2O$ and $CoSO_4,H_2O$ are known, each of which on heating loses its water forming an infusible, opaque mass of a rose-red colour.

Cobaltic sulphate, $Co_2(SO_4)_3,18H_2O$, is obtained when a cooled acid solution of cobaltous sulphate is electrolysed in a divided cell. It is deposited in blue needles soluble in water, which solution rapidly decomposes into cobaltous sulphate. It has also been prepared electrolytically by S. Swann, jun. and T. S. Xanthakos (J. Amer. Chem. Soc. 1931, **53**, 400), who have shown that it has strong oxidising properties towards many organic compounds.

Cobaltous nitrate, $Co(NO_3)_2$, in the anhydrous form, has been prepared by A. Guntz and F. Martin (Bull. Soc. chim. 1909, [iv], **5**, 1004) by the action of nitric anhydride or of a solution of nitric anhydride in nitric acid on hydrated cobaltous nitrate and also by the action of finely-divided metallic cobalt on a solution of silver nitrate in liquid ammonia. In this form it is a slightly pink powder which begins to decompose at 100°–105°. The hydrated nitrate, $Co(NO_3)_2,6H_2O$, is obtained by dissolving the oxide, hydroxide, or carbonate in dilute nitric acid, when a carmine red solution is obtained and on evaporation this furnishes reddish-brown deliquescent crystals. Other hydrated nitrates containing nine and three molecules of water have been prepared. Cobalt nitrate solution is used as a reagent in blowpipe analysis.

USES OF COBALT SALTS IN PAINTS AND VARNISHES.—Certain cobalt salts, such as the acetate, borate, resinate, oleate, linoleate, "oleo-resinates," benzoate, "tungtate," and cobalt as hydroxide are used as driers in the manufacture of paints and varnishes. Organic salts of cobalt have been found to be the most convenient and efficacious driers and have the additional advantage of causing no discoloration of the paint. To some extent cobalt salts also enable the lower-priced semi-drying oils such as soya, fish, and even cotton-seed oils to be substituted for the higher-priced linseed oil in the preparation of paints. The driers in the liquid and solid forms are also used in the manufacture of waterproof fabrics, linoleum, oilcloth, patent-leather, artificial leathers and similar industries.

When the acetate is used for drying linseed oil, from 0·2 to 0·4% is necessary. The oil is heated at 150°–200° and the acetate is stirred in until dissolved. Soya oil is treated similarly.

The borate is prepared by adding a solution of cobalt sulphate to a cold solution of borax; the precipitate formed is filtered washed with cold water, and dried.

The benzoate is prepared by adding cobalt carbonate to a solution of benzoic acid until neutral; the filtered and dried product is ground to powder.

For the preparation of the resinate the best American water-white rosin is used which should be completely soluble in turpentine and ether, have a melting-point of 75°–85°, and a saponification value of 167–180. The resinate may be prepared either by the precipitation or the fusion method. For the precipitation method the resin, suspended in water, is heated to 100° and a 20% solution of sodium hydroxide is gradually added with stirring. A solution of sodium chloride is then added to the clear brown solution. The precipitate of sodium resinate is dissolved in hot water and a 10% solution of cobaltous chloride is added to precipitate the sage-green cobalt resinate which is washed and dried. The fused resinate is prepared by heating the resin to 140° and adding cobalt hydrate with constant stirring. The temperature is then raised to 170°–180° and the melt poured into pans and allowed to cool. The precipitated resinate contains about 7·5% cobalt and the fused resinate 4–4·25%.

The fatty acid driers are usually made with linseed oil, although other oils, such as soya, tung or walnut, are sometimes used. The linseed oil is completely saponified by gradually adding 10% sodium hydroxide to the oil heated to 100°. The clear brown solution is then diluted with hot water and a solution of sodium chloride added. The granular soap formed is removed, redissolved in water, and reprecipitated with brine. The purified soap is again dissolved in water and a 10% solution of cobaltous chloride solution added. The precipitated cobalt "linoleate" is filtered, washed, and dried at 80°.

When 1·5% of a good drier is dissolved in linseed oil at a temperature of about 120° it should cause a thin film of this oil to dry at room temperature to a removable skin in 7–8 hours (*cf.* T. H. Gant, *l.c.*).

C. O. B.

COBALT BLOOM. Erythrite, hydrated cobalt arsenate, $Co_3As_2O_8,8H_2O$. It is found frequently as a peach-coloured incrustation on arsenical ores, being produced by their decomposition.

COBALT BLUE or THENARD'S BLUE *v.* COBALT, this vol. 218*c*.

COBALT BROWN, BRONZE, GREEN, RED, YELLOW *v.* COBALT, this vol. p. 219*c*.

COBALT-GLANCE, SULPHARSENIDE OF COBALT *v.* COBALTITE.

COBALT PYRITES, LINNÆITE *v.* COBALT., this vol. p. 214*b*.

COBALT SPEISS *v.* COBALT, this vol. 214*d*.

COBALTITE or COBALT-GLANCE. Sulpharsenide of cobalt, CoAsS, containing Co 25–35%, with Fe 2–5%. It frequently occurs as well-developed crystals, fine specimens coming from Tunaberg and Håkansboda in Sweden and Skutterud in Norway; these are cubic with parallel hemihedrism and with the same characteristic form as crystals of the isomorphous mineral iron-pyrites. Granular and compact masses also occur. The colour is tin-white with a reddish tinge and a brilliant metallic lustre; the streak is greyish-black. Sp.gr. 6·2, hardness 5½. A bed of pure cobaltite averaging 0·2 in. in thickness occurs at Dashkessan, Govt. Tiflis, Caucasus. In the Cobalt area of Ontario massive cobaltite and small crystals are present with the more abundant smaltite. Under the name *sehta* the mineral, found at Kherti, in Rajputana, is used by the Indian jewellers for producing a blue enamel on gold and silver.

L. J. S.

COBLAC *v.* CELLULOSE PLASTICS.

COCAINE AND OTHER ALKALOIDS OF ERYTHROXYLUM SPECIES. The genus *Erythroxylum* (Fam. Erythroxylaceæ) is principally found on the western side of South America, although indigenous species occur in India, Africa and Australia. Chiefly three kinds, derived originally from Bolivia and Peru, are cultivated:

1. *Erythroxylum coca.*
2. *E. coca*, var. *novogranatense* (=*E. carthagense* Jacq.).
3. *E. truxillense* Rusby (*E. Spruceanum*).

On the London market four kinds of coca leaves are distinguished: Huanuco (Bolivian, from 1); Truxillo (Peruvian, from 3); Java (from 2); Ceylon (from 2 or 3).

The alkaloids obtained from coca leaves fall into four groups, viz.:

1. The *cocaines*, which on hydrolysis yield ecgonine, methyl alcohol and benzoic, cinnamic, or truxillic acids:

Cocaine: Methyl benzoylecgonine.
Cinnamylcocaine: Methyl cinnamoylecgonine.
α-Truxilline (γ-isatropylcocaine): Methyl α-truxilloylecgonine.
β-Truxilline (δ-isatropylcocaine): Methyl β-truxilloylecgonine.

2. The *pseudotropeïnes* are closely related to the tropeines and are hydrolysed into pseudo tropine and an acid.

Tropacocaine: Benzoylpseudotropine.

3. The *acylecgonines* in which the carboxyl-group is free and only the alcoholic group is esterified:

Benzoylecgonine.

4. The *hygrines*, which are derived from pyrrolidine:

Hygrine and Cuscohygrine.

The two most important producing countries of coca are Bolivia and Java, but it is difficult to judge the world production of coca-leaves. In South America a considerable amount of crude cocaine is manufactured which does not come into the following statistics.

Export of Coca Leaves (From the Annual Reports of the League of Nations (nos. in kgs.):

	1932	1933	1934	1935	1936
Bolivia	347049	335807	205011	170189	131955
Dutch Indies	209131	161591	104671	125155	117264
Formosa	?	44598	44598	64598	49598
Peru	85542	76776	72374	89721	167896

Within the last years the coca production has much decreased, in 1924 Java produced as much as 1,071,000 kg. At the same time the number of coca plantations has decreased from 112 to 57 and the cultivated area from 2,112 to 864 hectares. Details of the production may be obtained from the Annual Reports of the League of Nations. The total alkaloid content of Java leaves is higher than the total alkaloid in South American coca. In different years the yield of total alkaloids varies considerably (Java, 1908: 1–2·5%; 1909: 1·22%). 90% of total alkaloids present in South American coca is *l*-cocaine, Java coca contains only 0·5% cocaine, the same percentage of cinnamyl-cocaine, and approximately 1% of truxillines, but these alkaloids can easily be transformed into *l*-cocaine. Coca-leaves experimentally grown in India contained 0·4–0·8% total alkaloids, chiefly cocaine (quoted by Henry, "Plant Alkaloids," 2nd ed., 1924, p. 96). The market for Java coca is Amsterdam; the London and Hamburg markets deal mostly with coca-leaves of other origin and with crude cocaine.

The coca plant is a shrub which, when carefully cultivated, can be grown for about 20 years. The leaves are plucked in the early morning and must be dried and ground the same day; they are then packed and shipped in tin boxes, avoiding any access of moisture, which is deleterious to the alkaloid content (*see* Martell, Pharm. Zentr. 1928, **69**, 551).

For history of coca, botanical details, cultivation, etc., *see* Tschirch "Handbuch der Pharmakognosie" (Leipzig, 1923, vol. III, 1, pp. 309–326).

Extraction of Coca.—Either coca-leaves or crude cocaine of South American origin are extracted. The general outlines of the extractions are known, but many details, *e.g.* the use of solvents and the preparation of different cocaine salts, are kept secret by the manufacturers.

The leaves are either extracted with dilute acids (*see* Ullmann, "Enzyklopädie der technischen Chemie," Berlin, 1929, vol. III, p. 453) or moistened with lime water or soda-solution and exhausted with Et_2O or benzene (*see* Duilius, Chem.-Ztg. 1930, **54**, 31, or Schwyzer, "Die Fabrikation der Alkaloide," Berlin, 1927, pp. 85ff). Also extraction processes with $H_2SO_4 + EtOH$ as solvents (Squibb) and many other modifications are known.

(*a*) Extraction suitable for Java coca: The leaves are exhausted with dilute H_2SO_4; after careful addition of soda the total alkaloids are extracted with benzene or toluene. Extraction of these solvents with 10% H_2SO_4 yields a solution of the crude total sulphates. The total alkaloids are hydrolysed with a small excess of dilute H_2SO_4 (boiling for 12–18 hours), when $MeOH$, benzoic, cinnamic, truxillic acids, and ecgonine are formed. The acids are removed and the mother-liquors concentrated; from the concentrated solution ecgonine is precipitated by $EtOH$. Thus all ecgonine present as cocaine, cinnamylcocaine, and the truxillines is available for the subsequent "synthesis" of cocaine. Ecgonine is first esterified with $MeOH$ and H_2SO_4, and then benzoylated with benzoyl chloride or benzoic acid+$POCl_3$.

(*b*) Extraction suitable for South American coca: The leaves are moistened with limewater and extracted with Et_2O. Dilute acetic acid extracts the total alkaloids from the ethereal solution. Crude cocaine is precipitated with soda-solution. This is dissolved in approx. 10% acetic acid, and at a temperature not exceeding +5° impurities are oxidised with permanganate until the red colour persists for 30 minutes. The solution is then neutralised with ammonia and the total alkaloids precipitated with 5% soda-solution. The dried precipitate, which is brown in colour, is dissolved in Et_2O and manganese dioxide filtered off. The ethereal solution is concentrated, when pure cocaine crystallises out. The mother-liquors are completely freed from Et_2O and treated with light petroleum, which dissolves any cocaine still present. The residue consists largely of isatropylcocaine, which is hydrolysed and transformed into cocaine as mentioned above.

Analyses of Coca-leaves.—The official "Amsterdam-analysis" of coca-leaves is not published, the values obtained include cinnamyl-cocaine and truxillines. In London and in Hamburg the content of crude cocaine is given according to the methods of Harrison and of Gilbert. The estimation is based on the extraction of the leaves with a mixture of Et_2O, $CHCl_3$ and ammonia. The organic solvents are then exhausted with dilute H_2SO_4 and the basified solution re-extracted with Et_2O. The evaporated extract is dissolved in excess of $N/10$ H_2SO_4 and titrated back with $N/50$ KOH using cochineal or iodeosin as indicator (*see* "United States Pharmacopœia," 8th Rev.). Other descriptions use light petroleum as extraction medium; the further process is similar, the alkaloids from the ethereal solution being dried to constant weight and then weighed. *See also* critical survey of Bierling, Pape and Viehöver (Arch. Pharm. 1910, **248**, 303) and de Jong (Arch Pharm. 1911, **249**, 209).

For microchemical identification of cocaine in plant material, *see* Klein and Sonnleithner

(Oesterr. Bot. Zeitschrift, 1927, **76**, 263) and Brandstetter (Chem. Zentr. 1922, IV, 729).

Official in the "British Pharmacopœia," 1932, are: Cocaine and Cocaine·HCl; official cocaine-containing prescriptions are: Lamella Cocainæ and Lozenge of Krameriæ et Cocainæ.

Official in the "United States Pharmacopœia," 1936, are: Cocaine and Cocaine·HCl.

Cocaine (I), $C_{17}H_{21}O_4N$, $[\alpha]_D^{20}$ −16·4° (in $CHCl_3$), m.p. 98°, volatile above 90°, crystallises from EtOH in monoclinic, four- to six-sided prisms. It is easily soluble in EtOH (1 part in 10 parts), Et_2O (1 : 4), benzene, carbon-disulphide, $CHCl_3$ (1 : 0·5), acetone and light petroleum, slightly soluble in H_2O (1 : 600). The saturated aqueous solution is alkaline to litmus, has a slightly bitter taste, and produces numbness when applied to the tongue.

(I) is precipitated from solutions of its salts by ammonia, caustic alkalis, and alkali carbonates. When (I) is boiled with H_2O benzoylecgonine and MeOH are produced; hydrolysis with mineral acids and with caustic alkali yields l-*ecgonine* (II) and d-*pseudoecgonine* respectively, together with MeOH and benzoic acid. Alkaline hydrolysis is 1,500 times more rapid than acid hydrolysis.

For dissociation constants of (I) and (II), *see* Kolthoff (Biochem. Z. 1925, **162**, 309–12). For test for identity and purity, *see* "British Pharmacopœia," 1932, p. 124, and "United States Pharmacopœia," 1936, p. 123.

Cocaine Hydrochloride is the salt chiefly used in medicine. It crystallises from EtOH in short prisms, $[\alpha]_D$ −71·95° (in 2% aqueous solution), m.p. 200–202°. The salt is soluble in 0·5 parts of H_2O and in 3 parts of 90% EtOH. Test for purity ("British Pharmacopœia," 1932): to 5 millilitres of a 2% aqueous solution add 0·3 millilitres of *N*/1 H_2SO_4 and then 0·5 millilitres of *N*/50 permanganate solution; a clear violet colour is produced, which in the absence of dust and at a temperature not exceeding 20° does not completely fade within 30 minutes (limit of reducing substances and of cinnamylcocaine). Similar test for purity in "United States Pharmacopœia," 1936.

Maclagan's Test: If a 10% ammonia solution is added to a solution of pure (I)·HCl, a crystalline precipitate of (I) must slowly be formed, a milky appearance indicates the presence of amorphous alkaloids, especially truxillines (for details of test and other tests, *see* "British Pharmacopœia" and "United States Pharmacopœia"). Cocaine does not give characteristic colour-reactions; for Vitali's colour-reaction, *see* Hardy (J. Pharm. Chim. 1921, [vii], **24**, 325).

OTHER SALTS: (I)·H_2CrO_4,H_2O, m.p. 127°, sparingly soluble in H_2O, is produced when potassium chromate is added to an acid solution of (I)·HCl. Other sparingly soluble salts are $B_2{\cdot}H_2PtCl_6$, $B{\cdot}HCl{\cdot}HgCl_2$, $B{\cdot}HI{\cdot}I_2$ (periodide), etc. (I)·HCl forms sparingly soluble precipitates with Mayer's reagent, phosphomolybdic, phosphotungstic and silicotungstic acids (*see* Rosenthaler, "Der Nachweis organischer Verbindungen," 2nd ed., p. 732).

For quantitative estimation of (I) and (I)·HCl, *see* Heikel (J.C.S. 1909, **96**, II, 104); Nyman-Björksten (Z. anal. Chem. 1915, **54**, 62); Garsed and Collie (J.C.S. 1901, **89**, 675); Klein ("Handbuch der Pflanzenanalyse," Wien, 1933, vol. IV, part 3/1, p. 540). (I) may be identified by the absorption-spectrum, Brustier (A. 1927, 91); Eisenbrand (Amer. Chem. Abstr. 1926, **20**, 2722); Castille and Ruppol (A. 1928, 920); Bontempi (Amer. Chem. Abstr. 1932, **26**, 1862); Fischer (*ibid.* 1933, **27**, 4552).

***d*-Cocaine** (*d*-ψ-cocaine) has been isolated from coca-leaves by Liebermann and Giesel (Ber. 1890, **23**, 508, 926). The alkaloid is probably not natural but formed during the extraction. $[\alpha]_D$ +42·2° (in $CHCl_3$), m.p. 46°, gives a sparingly soluble nitrate.

Cinnamylcocaine (III), $C_{19}H_{23}O_4N$, $[\alpha]_D$ −4·7° (in $CHCl_3$), m.p. 121°, crystallises from a mixture of benzene and light petroleum in rosettes of needles. (III)·HCl,$2H_2O$, m.p. 176° (dry), flattened needles from H_2O, platinichloride, m.p. 217°, aurichloride, m.p. 156°. When (III) is warmed with HCl, it is hydrolysed to *l*-ecgonine, cinnamic acid, and MeOH.

Truxillines (isatropylcocaines), $C_{38}H_{46}O_8N_2$. Hesse (Ber. 1889, **22**, 665) and Liebermann (Ber. 1888, **21**, 2342) isolated from Peruvian coca-leaves two amorphous alkaloids which were first named *cocamine* and *isococamine*.

α-Truxilline (IV) (cocamine, γ-isatropylcocaine): amorphous white powder, m.p. 80°, easily soluble except in light petroleum.

β-Truxilline (V) (*iso*cocamine, δ-isatropylcocaine): amorphous, sinters at 45° and decomposes at 120°. Both truxillines on acid hydrolysis yield ecgonine, MeOH, and α- or β-truxillic acids $(C_9H_8O_2)_2$ respectively.

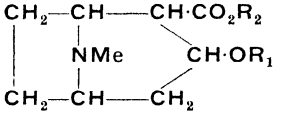
Benzoylecgonine, $C_{16}H_{19}O_4N$, $[\alpha]_D$ −63·3° (in H_2O); crystallises from water with $4H_2O$ in needles, m.p. 92° or 195° (dry). It is obtained by boiling (I) in H_2O. It was also obtained in small amounts from coca-leaves (*see* Skraup, Monatsh. 1885, **6**, 556).

***l*-Ecgonine** (II), $C_9H_{15}O_3N{\cdot}H_2O$, $[\alpha]_D$ −45·4° (in H_2O), m.p. 198° (anhydrous), crystallises from dry alcohol in monoclinic prisms with $1H_2O$, easily soluble in H_2O, less in EtOH, insoluble in Et_2O, $CHCl_3$, and other organic solvents. (II) is the final basic hydrolytic product obtained by action of *acids* on the cocaines (*see* introduction); it is an amphoteric substance and when esterified with MeOH and benzoylated, (I) is obtained. By variation of the acid chlorides and the alcohols, many homologues of (I) have been prepared.

***d*-Ecgonine** (better *d*-ψ-ecgonine) is dextrorotatory, m.p. 254° (264°); it crystallises from dry EtOH in tablets. *d*-ψ-Ecgonine is formed when the cocaines are hydrolysed by alkalis. *d*-ψ-Ecgonine is not an optical but a stereoisomeride of (II). Like the latter, it forms a series of esters; from *d*-ψ-ecgonine *d*-cocaine (methyl benzoyl-*d*-ψ-ecgonine) has been prepared.

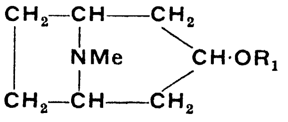
Tropacocaine (VI) (Benzoyl-ψ-tropeine) $C_{15}H_{19}O_2N$, has been found in Java and Peruvian coca-leaves (Giesel and Liebermann, Ber. 1891, **24**, 2336; *cf. also* Reens, Chem. Zentr. 1920, IV, 103). (VI) is optically inactive, m.p. 49°, it crystallises in needles, soluble in EtOH and Et_2O, insoluble in H_2O. When heated with HCl or baryta it is hydrolysed to benzoic acid and ψ-tropine (m.p. 108°, b.p. 240°) which is a stereoisomeride of tropine since it can be oxidised to tropinone. Tropine and ψ-tropine are mutually convertible. Dissociation constants of (VI), *see* Kolthoff (Biochem. Z. 1925, **162**, 307). Analytical differences between (I) and (VI) *see* Reichard (Pharm. Zentr. 1908, **49**, 337). For synthesis of a ring-homologue of (VI), *see* Blount and Robinson (J.C.S. 1932, **1429**). (VI), under the form of the hydrochloride, is the only other coca-alkaloid used in medicine.

Constitution of the Cocaines.—The cocaines are esters of the amphoteric substance ecgonine with MeOH and benzoic, cinnamic, or truxillic acid. Ecgonine and its derivatives differ throughout from tropine and its derivatives by $\mathrm{CO_2}$. A derivative of ecgonine (anhydro ecgonine) was transformed into a derivative of tropine (tropidine) (Einhorn, Ber. 1890, **23**, 1338); this fact proved that (II) is a tropine carboxylic acid. This is also confirmed by Willstätter's degradation of (II) to suberone. The elucidation of the tropine-structure led Willstätter (Ber. 1898, **31**, 1202, 2655) to propose the following structures for (II) and its derivatives:

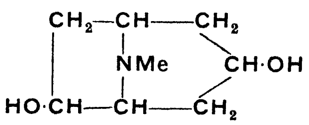


(II): $R_1=R_2=H$.
(I): $R_1=C_6H_5\cdot CO$; $R_2=Me$.
(III): $R_1=C_6H_5\cdot CH{:}CH\cdot CO$; $R_2=Me$.
(IV) and (V): $R_1=(C_9H_8O_2)_2$; $R_2=Me$.

Formula (B) represents (VI). Wolfes and Hromatka (Amer. Chem. Abstr. 1935, **29**, 4365) have isolated an interesting new tropane-derivative from coca-leaves for which they suggest the formula (C):



(B) $R_1=C_6H_5\cdot CO$.

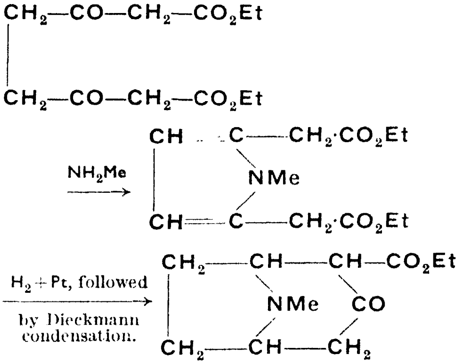


(C.)

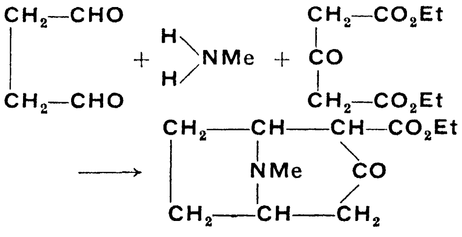
Syntheses of Cocaine.—There are four stereoisomerides of ecgonine and cocaine possible, three of which have been obtained synthetically. *r*-Ecgonine and *r*-ψ-ecgonine have been resolved into *d*- and *l*- forms. These two forms differ in the spatial arrangement of the hydroxyl-group (cis-trans-isomerism as in tropine and ψ-tropine); the third form which has not been resolved differs by the cis-trans-isomerism of its carboxyl-group. (For theoretical discussion, *see* Willstätter and Bommer, Annalen, 1921, **422**, 18).

1. Willstätter and Bode (Ber. 1901, **34**, 1457; Annalen, 1903, **326**, 42) obtained sodium tropinone carboxylate by interaction of sodium tropinone with $\mathrm{CO_2}$ and sodium. This on reduction with sodium amalgam in weakly acidic solution gave a mixture of *r*-ψ-ecgonine and *r*-ecgonine (*see* additional note, Willstätter, Wolfes, and Mäder, Annalen, 1923, **434**, 134).

2. A second synthesis of *r*-ψ-ecgonine is described by Willstätter and Bommer (Annalen, 1921, **422**, 15): Diethyl succinyldiacetate is condensed with methylamine, the resulting pyrrole-derivative is catalytically reduced to a pyrrolidinedicarboxylate which by a Dieckmann condensation is transformed into tropinonecarboxylic ester. This ester is identical with the product of synthesis 1.



3. From the technical point the third synthesis of Willstätter, Wolfes, and Mäder (*l.c.*) is the most valuable. Succinic dialdehyde, methylamine and the dipotassium salt of ethyl acetonedicarboxylate are condensed to yield ethyl tropinonecarboxylate (*cf.* Robinson, J.C.S. 1917, **111**, 762).

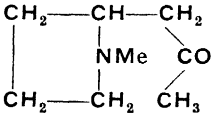


Reduction of the last substance yielded *r*-ψ-ecgonine (1), *r*-ecgonine, (2) and the third racemic ecgonine (cis-trans-isomeric tropanolcarboxylic acid). On resolution (1) yielded *d*- and *l*-ecgonine, the former, on esterification with MeOH and benzoylchloride gave *d*-cocaine (*d*-ψ-cocaine, *see* earlier). The bitartrate of *d*-ψ-cocaine is called *psicaine*, it is also used as local anæsthetic and is a product of some importance. If (2) is resolved and esterified *d*- and *l*-cocaine are obtained, the latter is identical with natural cocaine.

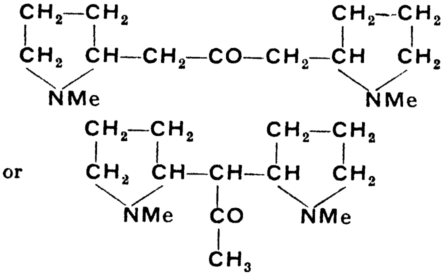
Hygrines.—The hygrines were discovered by Lossen (Annalen, 1862, **121**, 374) in Peruvian coca-leaves. Liebermann showed that this alkaloid fraction by distillation *in vacuo* can be separated into the two alkaloids hygrine and cuscohygrine.

Hygrine (VII), $C_8H_{15}ON$, $[\alpha]_D-1{\cdot}3°$, b.p. 92–94°/20 mm. or 193–195°/760 mm., is a strongly alkaline liquid, yielding a characteristic picrate, m.p. 158°, and a crystalline oxime, m.p. 116–120°. By oxidation with CrO_3 *hygric acid* ($C_6H_{11}O_2N$) is obtained which was synthesised by Willstätter (Ber. 1900, **33**, 1160; Annalen, 1903, **326**, 91). *r*-Hygrine was synthesised by Hess (Ber. 1913, **46**, 3113, 4104).

Cuscohygrine, $C_{13}H_{24}ON_2$ (VIII), is optically inactive, b.p. 185°/32 mm., forms a crystalline oxime, m.p. 53–54°, is miscible with H_2O, a crystalline hydrate is known (m.p. 40°), and the salts are crystalline. The nitrate is characteristic, it crystallises from EtOH, m.p. 209° (decomp.). (VIII) is very labile; by influence of acids or alkalis it is easily transformed into (VII); when oxidised with CrO_3, hygric acid (*N*-methylpyrrolidine-2-carboxylic acid) is obtained. Various papers deal with the constitution of (VIII), but no final decision can be taken between the two possible alternatives (*see* Hess and co-workers, Ber. 1915, **48**, 1986; 1920, **53**, 781; 1921, **54**, 2310; Annalen, 1925, **441**, 137).



VII.



VIII.

Physiological Action of the Cocaine-Group.—Cocaine is used in medicine as a local anæsthetic, it is mydriatic and highly toxic. It acts chiefly on the central nervous system, death occurs from paralysis of the respiratory centre. Tropacocaine is the only other coca-alkaloid used in medicine. For psicaine, *see* Gottlieb (Z. physiol. Chem. 1923, **130**, 374). For details of cocaine action, *see* Henry, "Plant Alkaloids," 2nd ed., p. 112, and text-books of pharmacology.

Schl.

COCAMINE *v.* Cocaine, (this vol. p. 224*c*).

COCCERIC (COCCERINIC) ACID *v.* Cochineal Fat and Wax.

COCCERIN or **COCCERYL COCCERATE.** A wax extracted from Cochineal insects (*v.* Cochineal Wax and Fat).

COCCERYL ALCOHOL *v.* Cochineal Fat and Wax.

COCCINE *v.* Cochineal, (this vol. p. 228*d*).

α-COCCINIC ACID, COCCININ *v.* Cochineal.

COCCININ *v.* Cochineal, (this vol. p. 228*d*).

COCCINONE *v.* Cochineal, (this vol. p. 228*d*).

COCCULUS INDICUS or **INDIAN BERRY** *v.* Anamirta Paniculata.

COCHENILLIC ACID *v.* Cochineal, (this vol. p. 228*b*).

COCHINEAL. This natural dyestuff was used as a dye and cultivated by artificial means in its native country, Mexico, at a remote period of history. Cochineal consists of the dried body of an insect, the *Coccus cacti*, which lives upon a species of cactus (the *Nopalea coccinellifera* S.-Dyck or *Nopal*), a plant which is found in the wild condition, but which, for the sake of the insect, is cultivated in gardens which are termed *Nopaleries*. The insects are collected before the commencement of the rainy season, and are killed by immersion in boiling water, or are enclosed in a linen bag and placed in an oven ; by the latter process the peculiar white down covering the insect is preserved, but in the former case is lost.

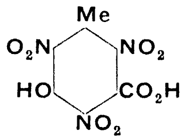
In Mexico and Central America two varieties of cochineal are known—the home-grown or fine cochineal (*grana fina*), and the wild or forest cochineal (*grana silvestra*). The former is more valuable than the latter, and is richer in colouring matter. After 1830 the cultivation of cochineal was introduced into Spain and the Canary Islands, Algeria and Java, but the most productive of these newer plantations were those of Java. Since the discovery of the coal-tar colours, the consumption of cochineal as a dyestuff has gradually decreased, and at the present time it is only employed in a minor degree. According to Liebermann (Ber. 1885, **18**, 1969) cochineal contains about 10% of colouring matter.

Carminic acid, the colouring matter of cochineal, was first isolated by Pelletier and Caventou (Ann. Chim. Phys. 1818, [ii], **8**, 250) and was subsequently examined by many chemists. Schützenberger (*ibid.* 1858, [iii], **54**, 52) succeeded in obtaining carminic acid in a crystalline condition by precipitating the colouring matter as its lead compound, decomposing this with hydrogen sulphide, and crystallising the liberated carminic acid from alcohol-ether. The most simple method of purification of carminic acid, however, is that devised by Miller and Rohde (Ber. 1897, **30**, 1762). A solution of the crude colouring matter in five times its weight of water is diluted with four times its volume of acetic acid ; the filtered liquid, on standing over sulphuric acid, gradually deposits the carminic acid in a crystalline condition.

Carminic acid crystallises in red prisms easily soluble in water and alcohol with a purple-red colour. It possesses no melting-point, but darkens at 130°, and at 250° becomes quite black. Of the many empirical formulæ suggested for carminic acid by earlier workers, that advanced by Liebermann, Höring and Wiedermann (Ber. 1900, **33**, 149), viz. $C_{22}H_{22}O_{13}$, was generally accepted as correct. More recently Dimroth has modified this expression to $C_{22}H_{20}O_{13}$.

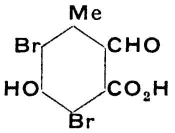
By the action of alcoholic potassium acetate, Perkin and Wilson (J.C.S. 1903, **83**, 139) prepared a *mono-* and a *di-* potassium salt, whilst Liebermann, Höring and Wiedermann (*l.c.*) obtained *hexabenzoylcarminic acid* as an orange-coloured powder, easily soluble in benzene. *Octa-acetylcarminic acid*, golden-yellow needles, melting gradually at 155–165°, is readily prepared by the action of acetic anhydride in presence of zinc chloride or sulphuric acid (Miller and Rohde, *l.c.*).

Constitution of Carminic Acid.—By the prolonged action of boiling nitric acid on carminic acid, W. de la Rue obtained *nitrococcussic acid*, which was subsequently shown by Kostanecki and Niementowski (Ber. 1885, **18**, 250) to be identical with trinitrocresotinic acid :

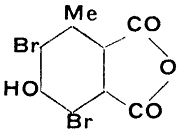


When carminic acid, dissolved in 50% acetic acid, is treated with an excess of bromine, and the solution digested at the boiling heat, two substances, *a-* and *β-bromocarmines*, are produced (Will and Leymann, Ber. 1885, **18**, 3180).

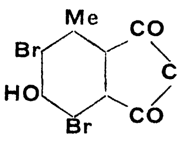
a-Bromocarmine, $C_{10}H_4Br_4O_3$, colourless needles, m.p. 247–248° (decomp.), the more sparingly soluble substance, when oxidised with potassium permanganate in alkaline solution gives dibromomethylhydroxyaldehydobenzoic acid and dibromomethylhydroxyphthalic anhydride :



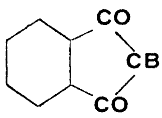
and



Miller and Rohde (Ber. 1893, **26**, 2663) observed that when *a*-bromocarmine is treated with hot caustic soda solution it yields, in addition to a purple-red colouring matter, dibromomethylhydroxyphthalic acid and bromoform. As a result of this reaction, these authors assigned to *a*-bromocarmine the constitution of a methylhydroxytetrabromodiketohydrindene (I), for Zincke (Ber. 1887, **20**, 3227 ; 1888, **21**, 2388) had previously shown that dibromodiketohydrindene (II) under similar treatment yields both phthalic acid and bromoform.

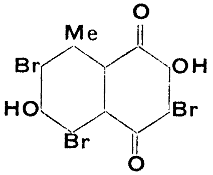


I.



II.

β-Bromocarmine, $C_{11}H_5Br_3O_4$, crystallises from acetone in orange needles, m.p. 232° (Will and Leymann) or 238° (Miller and Rohde), and is converted into *a*-bromocarmine by the action of bromine in 50% acetic acid solution. As a result of their investigation, Miller and Rohde ascribed to *β*-bromocarmine the constitution of a methyldihydroxytribromo-*a*-naphthaquinone (III or IV). This suggestion was supported by the fact that bromohydroxynaphthaquinone (V), on treatment with bromine and caustic soda solution, is converted into dibromodiketohydrindene (II) (Zincke, *l.c.*). Further support for this view was obtained by Rohde and Dorfmüller (Ber. 1910, **43**, 1363), who found that by reduction with zinc dust and acetic acid and subsequent acetylation, *β*-bromocarmine gives the compound (VI), colourless needles, m.p. 208°. Simultaneous hydrolysis and oxidation converts this into the substance (VII), orange prisms, m.p. 258° ; and it thus appears that by the latter treatment an hydroxyl group has entered the quinone nucleus. The diacetyl derivative melts at 233°. When distilled with zinc dust, this product, and also *β*-bromocarmine itself, give naphthalene.



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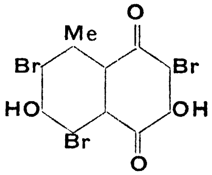

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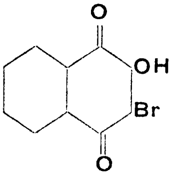

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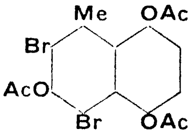

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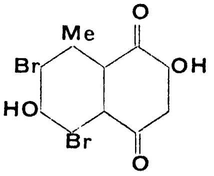
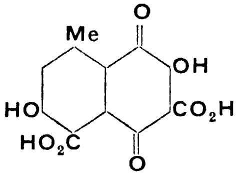
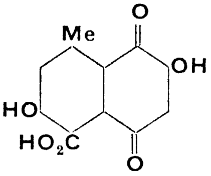


VII.

Subsequently, Dimroth (Annalen, 1913, **399**, 1) oxidised carminic acid with hydrogen peroxide in aqueous caustic soda, using cobalt sulphate as a catalyst, and obtained 2:6-dihydroxy-8-methyl-*a*-naphthaquinone-3:5-dicarboxylic acid (VIII) which he orientated by comparing its colour reactions with those of synthetic 2:6-dihydroxy-*a*-naphthaquinone, and also by its conversion into carminazarin (XIV) by treatment with acid permanganate. When (VIII) is warmed with water, carbon dioxide is eliminated with the production of 2:6-

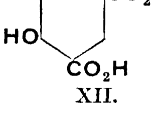
dihydroxy-8-methyl-α-naphthaquinone-5-carboxylic acid (IX). This compound, when brominated in glacial acetic acid at 40°, yields the 7-monobromo- derivative which on treatment with hydrobromic acid gives α-bromocarmine, whilst with bromine in cold methyl alcohol the product is β-bromocarmine, which thus has the structure (III) assigned to it by Miller and Rohde.

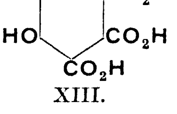

VIII.


IX.

Liebermann and Voswinckel (Ber. 1897, **30**, 688, 1731) studied the oxidation of carminic acid with alkaline permanganate at the ordinary temperature, and in this way succeeded in producing two important acids, cochenillic (cochinelic or cochinillic) and α-coccinic acids.

Cochenillic acid, $C_{10}H_8O_7$, colourless needles, m.p. 224–225° with evolution of carbon dioxide, is tribasic and at 260° is converted into methyl hydroxyphthalic anhydride (X). When heated with water in a sealed tube at 210° it yields cresotinic acid (XI), and in the same manner at a lower temperature, 170°, gives α-coccinic acid (XII), the second product of the oxidation of carminic acid. *α-Coccinic acid*, $C_9H_8O_5$, colourless needles, m.p. 239°, proved to be identical with *m*-hydroxyuvitic acid (Oppenheim and Pfaff, Ber. 1874, **7**, 929). It thus follows that cochenillic acid has the formula (XIII).


X.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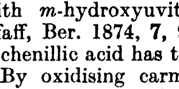
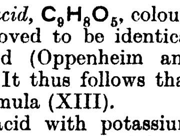
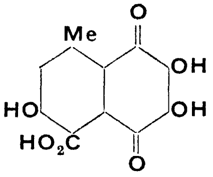
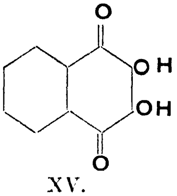

XII.


XIII.

By oxidising carminic acid with potassium permanganate at 0° in the presence of sulphuric acid, Dimroth (Ber. 1909, **42**, 1611) obtained ***carminazarin***, garnet-red needles, decomposing at 240–250°. It possesses the constitution (XIV) and is very similar to *iso*naphthazarin (XV). Its alkaline solution, when treated with a stream of oxygen, is quickly decolourised with formation of 5:6-dicarboxy-4-hydroxy-*o*-tolylglyoxylic acid (XVI). A further point of resemblance of carminazarin to *iso*naphthazarin is shown by its behaviour with nitric acid in glacial acetic acid, for whereas the latter gives tetraketotetrahydronaphthalene, the former yields the analogous *carminazarinquinone* (XVII) which, when heated with water or acetic acid, passes back to carminazarin. Carminazarinquinone is converted into a *diphenazin*, $C_{24}H_{14}O_3N_4$, by treatment with an alcoholic solution of *o*-phenylenediamine.


XIV.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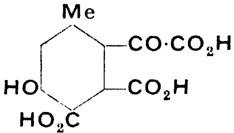
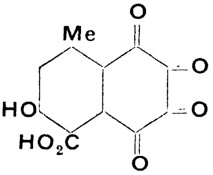
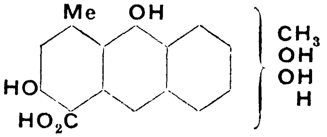

XVI.


XVII.

Coccinin, according to Hlasiwetz and Grabowski (Annalen, 1867, **141**, 329), is produced when carminic acid is fused with caustic potash. It crystallises from alcohol in straw-yellow needles or leaflets, dissolves in alkalis with a yellow colour which, by air oxidation, develops first a green, then violet, and, finally, a purple tint. Dimroth (Annalen, 1913, **399**, 1) examined this product in detail, preparing it by fusing carminic acid with caustic potash at 170–200°. To it he gave the formula $C_{17}H_{14}O_6$, and described the pale yellow crystalline *tetra-acetyl-* derivative, m.p. 242–244°. When coccinin was oxidised by air, or oxygen, in dilute sodium hydroxide solution, the colour changes above described occurred, and when the pure violet colour had been obtained, acidification yielded *coccinone*, $C_{17}H_{12}O_7$, dark brown glistening crystals, decomposing at 250° and yielding a *triacetyl* derivative, orange-red crystals, m.p. 210°. Coccinone is reconverted into coccinin by reduction with zinc dust and ammonia; on the other hand, alkaline oxidation by means of hydrogen peroxide below 20° gives rise to cochenillic acid. Dimroth thus formulated coccinin and coccinone as derivatives of anthranol and anthraquinone respectively, the production of cochenillic acid indicating the positions of the carboxyl and one hydroxyl and one methyl group:



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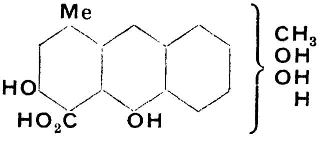
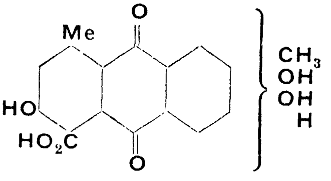


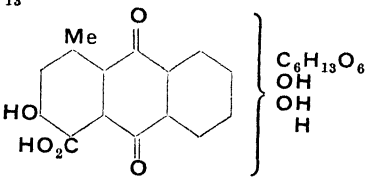
Coccinin.



Coccinone.

Dimroth further concluded that carminic acid itself is a derivative of anthraquinone, for by distillation with zinc dust in an atmosphere of hydrogen, a 5% yield of hydrocarbons of the anthracene series was obtained. After oxidation of the mixture of hydrocarbons he isolated anthraquinone, and possibly α-methylanthraquinone. Further, by treatment of carminic acid with boiling dilute sulphuric acid, a 10% yield of trihydroxymethylanthraquinone carboxylic acid was obtained, and this acid, when heated with water at 230–240°, yielded trihydroxymethylanthraquinone by loss of carbon dioxide. Dimroth therefore formulated carminic acid :

$C_{22}H_{22}O_{13}=$

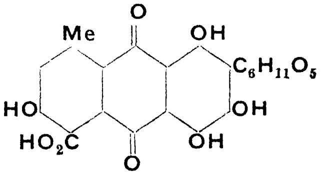


An examination of kermesic acid, the colouring matter of kermes, by Dimroth and Fick (Annalen, 1916, **411**, 315) showed that this acid is a derivative of hydroxyanthrapurpurin. The similarity of the absorption spectra and dyeing properties of kermesic acid to those of carminic acid led Dimroth and Kämmerer (Ber. 1920, **53**, [B], 471) to infer that the latter is also a derivative of hydroxyanthrapurpurin.

Under suitable conditions carminic acid is reduced by zinc dust and acetic acid to a leuco-compound which is converted by atmospheric oxidation into *deoxycarminic acid*, yellowish-red needles, the acetyl- derivative of which melts at 245–250° (decomp.). Deoxycarminic acid differs from carminic acid only in having one atom of oxygen less, due to the loss of the β-hydroxyl group in the purpurin nucleus during the reduction. That deoxycarminic acid contains two hydroxyl groups in the 1 : 4-position is shown by its oxidation to a diquinone, from which carminic acid is regenerated by the action of acetic anhydride and sulphuric acid. Parallel reactions are observed in the case of kermesic acid and hydroxyanthrapurpurin.

When carminic acid is warmed with acetic anhydride in the absence of a catalyst, a *hexa-acetyl* derivative is formed, and two hydroxyl groups in α-positions in the nucleus remain unacetylated, since the substance is readily oxidised to an unstable diquinone, reduced by sulphurous acid to the parent substance. With acetic anhydride and sulphuric acid at the ordinary temperature, carminic acid yields an *octa-acetyl* derivative. Since only four hydroxyl groups are present in the anthraquinone nucleus, it follows that the remaining four must be present in the side-chain, to which the composition $C_6H_{13}O_5$ has been previously assigned (Dimroth, Annalen, 1913, **399**, 13). This side-chain can only be a saturated univalent hydrocarbon radicle with five oxygen atoms, four only of which have been shown to be present as hydroxyl groups; hence it is concluded that the remaining oxygen atom is present in the ethereal, aldehydic, or ketonic form, and its formula must then be modified to $C_6H_{11}O_5$. Accordingly, the empirical formula for carminic acid becomes $C_{22}H_{20}O_{13}$, and an examination of recorded analyses showed that they agree as well with this as with the older formula. Hence carminic acid is :

$C_{22}H_{20}O_{13}=$



Carminic acid is optically active and has $[\alpha]_{645}^{15}$ $+51{\cdot}6°$ in aqueous solution This phenomenon cannot be attributed to the structure of the nucleus, since kermesic acid, and also the less closely related laccaic acid, are optically inactive ; it therefore appears that the side-chain contains at least one asymmetric carbon atom.

According to Miyagawa (Mem. Coll. Eng. Kyushu Imp. Univ. 1926, **4**, 99), carminic acid, when treated with ozone in aqueous solution, yields an optically active product from which, by oxidation, an optically active *acid*, $C_6H_{12}O_6$, is obtained. On reduction with sodium amalgam this acid yields a *sugar*, $C_6H_{12}O_5$, which is not identical with any of the known methylpentoses. The side-chain in carminic acid has thus the probable structure $CH_3{\cdot}[CH{\cdot}OH]_4{\cdot}CO$—.

Technical Preparations of Cochineal—Ammoniacal Cochineal, or *carminamide*, is prepared by allowing a solution of carminic acid in ammonia to stand for some time ; the clear liquid is decanted and evaporated with, or without, addition of gelatinous alumina. The product appears to consist of carminic acid in which one of the hydroxyls has been replaced by an amino-group.

Ammoniacal cochineal dyes much bluer shades than cochineal itself, and was sometimes used in conjunction with the latter; it also found some application in the blueing of bleached cotton.

Dyeing Properties of Cochineal.—Cochineal has been little employed in cotton dyeing, but was very largely used in silk and wool dyeing. It has now been practically replaced by the azo scarlets.

A crimson shade is produced on wool by mordanting with aluminium sulphate and cream of tartar and dyeing in a separate bath with cochineal, whilst a very fiery scarlet is obtained by the employment of stannous and sometimes stannic chlorides. For scarlet, wool can be mordanted with stannous chloride and tartar, and dyed in a separate bath with cochineal. A single-bath method, using stannous chloride, oxalic acid and cochineal, has, however, been very largely used for this purpose. On wool mordanted with chromium or iron, cochineal gives purple, slate or lilac colours, but these mordants are not employed in practice.

Cochineal red on wool possesses considerable fastness to light, but has the defect that weak alkalis and soap cause it to acquire a duller or more bluish shade.

Silk is dyed a good crimson shade by mordanting with alum and dyeing with an extract of cochineal. In scarlet dyeing, silk is preferably first dyed yellow, then mordanted with "nitromuriate of tin," and finally dyed in a second bath with the assistance of cream of tartar. Silk can also be dyed in a single bath with cochineal, indicator (Vol. II, p. 639*d*).

A. G. P. and E. J. C.

COCHINEAL FAT AND WAX. On extracting cochineal insects (*Coccus cacti*) with boiling benzene (Liebermann, Ber. 1885, **18**, 1975; Liebermann and Bergami, *ibid.* 1887, **20**, 959) or chloroform (M. Becker, Biochem. Z. 1931, **239**, 235) a fatty material, which can be separated into an alcohol- and ether-insoluble wax, *coccerin* (*c.* 0·5–4% of the dried insects) and the ether-soluble *cochineal fat* (*c.* 7–14% of the insects). The *fat*, as examined by Huerre (J. Pharm. Chim. 1911, **4**, 56) had an iodine value of 50 and an acid value of 89; it contained only 3% of unsaponifiable matter and yielded 8% of glycerol. The fatty acids appeared to consist of a mixture of myristic, oleic and linolic acids.

Coccerin (m.p. 99–103°C.) (*cocceryl coccerate*) was shown by Liebermann (*l.c.*) to be an ester of *cocceryl alcohol* with *cocceric* (*coccerinic acid*. **Cocceryl alcohol**, originally believed to be a C_{30} (Liebermann) or C_{32} (Becker) dihydric alcohol, has been identified by Chibnall and co-workers (Biochem. J. 1934, **28**, 313) as 15-keto-*n*-tetratriacontanol,

$$CH_3{\cdot}[CH_2]_{18}{\cdot}CO{\cdot}[CH_2]_{13}{\cdot}CH_2{\cdot}OH.$$

Correspondingly, **cocceric acid**, which was formerly thought to be a C_{31} or C_{32} hydroxy-acid, has been proved to be a mixture of 13-keto-*n*-dotriacontanoic acid,

$$CH_3{\cdot}[CH_2]_{18}{\cdot}CO{\cdot}[CH_2]_{11}{\cdot}COOH,$$

and *n*-triacontanoic acid, $CH_3{\cdot}[CH_2]_{28}{\cdot}COOH$ (Chibnall, *l.c.*, *cf. ibid.* 2189, 2209).

E. L.

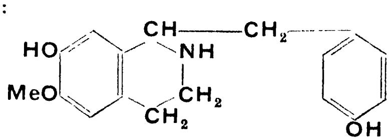
COCINIC ACID. A term now obsolete applied by Saint-Evre (Ann. chim. 1847, **20**, 99) to an acid, m.p. 34·7°C., supposed to be undecylic acid, separated from coconut oil. Like "*umbellulic acid*," which was isolated from the seed-fat of the Californian bay-tree (*Umbellularia californica* Nutt., Fam. *Lauraceæ*) by Stillmann and O'Neill (Amer. Chem. J. 1883, **4**, 206) and also believed to be an undecylic acid, "*cocinic acid*" appears to have been, in fact, an impure preparation of lauric acid (dodecylic acid). Undecylic acid ("cocinic acid") is also absent from chaulmoogra oil, in which its presence was reported by Moss (Pharm. J. 1879, **39**, 251).

E. L.

COCLAURINE is an important alkaloid, as it is the mother-substance of the whole group of the "biscoclaurine-alkaloids" (*cf.* Kondo and Tomita, Arch. Pharm. 1936, **274**, 65).

It was isolated from *Cocculus laurifolius* by H. Kondo and T. Kondo (J. Pharm. Soc. Japan, 1925, No. 524,876). It crystallises in colourless plates, m.p. 221°, $[\alpha]_D^{29}$ −17·01°, easily soluble in hot EtOH and acetone, sparingly so in cold EtOH, acetone, Et_2O, $CHCl_3$, insoluble in benzene and light petroleum.

B·HCl, needles, m.p. 264°; *methiodide* prisms, m.p. 155° (tri-acetyl and tri-benzoyl-compounds). By oxidation of the methine base, Kondo obtained oxalic, anisic, and a derivative of phthalic acid (Chem. Zentr. 1927, I, 2203). By ethylation of the phenolic OH-groups, H. Kondo and T. Kondo obtained degradation products which demonstrated conclusively the following structure (J. pr. Chem. 1930, [ii] **126**, 24):



For absorption-spectrum of coclaurine, *see* Kondo, Chem. Zentr. 1929, II, 752, 1012.

Schl.

COCOA. The cacao tree is an evergreen shrub indigenous to Mexico and the tropical regions of Central America, whence it was introduced into Europe by Cortes in 1528. It belongs to the family Sterculiaceæ and comprises several species, that most highly valued and cultivated being the *Theobroma Cacao*, so called by Linnæus, from θεός (god) and βρῶμα (food) in allusion to the esteem in which the beverage prepared from its seed was held by the natives of Central America, and to the Mexican name of the tree—*Cacouatl* or *Quacahault*.

Production.—The world production of cocoa has steadily increased, rising from 577,600 tons in 1931–1932 to 679,160 tons in 1934–1935. Of the latter total, the Gold Coast produced

258,400 tons and Brazil 98,700 tons. Other producing countries are Caracas, Central America, Ecuador, Essiquibo, Grenada, Guayaquil, Peru, Trinidad, Venezuela and the West Indies, Ceylon, East Indies, Philippines, Mauritius, Madagascar, San Thomé, Cameroons and the northern parts of Australia. The exportation of cocoa is of increasing importance in the trade of certain portions of the British Empire. Over 60% of the world trade is of imperial origin, whilst about 95% of the raw cocoa used in the United Kingdom comes from the Empire. The quantity of raw cocoa retained for home consumption in this country has increased from nearly 50,000 tons in 1926–1927 to over 70,000 tons in 1935–1936. The largest importing country in 1934 was the United States of America with 197,000 tons, Germany being second with nearly 100,000 tons.

Cultivation.—The cacao tree thrives only in tropical temperatures, in districts which are moist and sheltered from winds. Thus, those places where it is cultivated with success lie in latitudes between 25° north and south of the equator and at elevations seldom exceeding 1,000 feet. The soil affording best results is well drained, alluvial sandy loam. McDonald (Imp. Coll. Trin. 3rd Ann. Rep. 1933, p. 36) gives data relating to suitable and unsuitable soils in which the organic matter in good specimens varies between 2·8 and 4·0% whilst the available P_2O_5 is between 63 and 149 parts per million. Manuring is not often necessary although stable manure can be applied with advantage, and to sandy soils the addition of superphosphate in the proportion of 1–3 lb. per tree promotes fertility. Potassium fertilisers tend to increase the weight rather than the number of the beans. The tree usually grows to a height of about 25 ft., although occasionally it reaches 40 ft., but under cultivation it rarely exceeds 18 ft. It begins to bear fruit when 3 or 4 years old, attains full productivity in a further 4 or 5 years, and may be expected to bear for 40 or 50 years. Fruit is produced all the year round, but harvesting usually takes place only twice a year—from February to April and again in October and November. This requires great skill and judgment, as there is danger of the fruit being cut off too early or the flowers of the later crops being damaged. The fruit, which is suspended on a short thick stalk, consists of an elongated pod, varying in shape between a melon and a cucumber, measuring from 5 to 12 in. in length and 2–4 in. in diameter. Inside the pods are beans, varying in number from 20 to 40, and embedded in a rose-coloured mucilaginous pulp. The trees have been divided into three main classes, depending upon the fruit and other botanical differences : *Criollo, Forastero,* and *Calabacillo.* The first class, in which may be included those of Java and Ceylon, produces the finest type of beans, but the trees are more difficult to cultivate and are less regular in their yield of fruit. The wall of the pod is soft and thinner than the other varieties whilst the bean is less bitter. *Forastero* includes some of the best products of Central America. *Calabacillo* is the most easily cultivated. The pods are smaller whilst the beans are flat and have a more astringent taste than the other classes. When fresh the beans of all classes are usually white, although occasionally ranging through red to purple, but after drying and exposure to air and light they acquire a yellow, red, or brown colour and become hard, brittle, and less bitter.

Fermentation.—After removal from the pods the beans have to be freed from the adhering pulp. This is occasionally done by artificial or sun drying and subsequent rubbing and sorting. This method, however, produces a bitter product, quite unfit for the manufacture of chocolate or high-class cocoa. The usual procedure includes fermentation, which, whilst facilitating the removal of the pulp, improves the flavour and aroma of the final product. To promote fermentation the beans were formerly buried in the ground or in trenches covered with plantain leaves. Owing, however, to the adherence of earthy matter to the beans and the difficulty of control and handling, this process is not now generally employed. The beans are now placed in casks or boxes or heaped on the floors of sheds. The fermentation process usually lasts from 2 to 7 days, the temperature in that period rising to about 48°C. Care has to be taken to maintain an even temperature throughout the mass and this is achieved by shovelling the heaps periodically or transferring from one container to another. The process of fermentation is first alcoholic, owing to the action of a yeast fungus *Saccharomyces Theobroma* Preyer, and later acetic, set up by *Mycoderma aceti.* F. L. Stevens (Bull. Dept. Agric. Trinidad and Tobago, 1925, **21**, Part 1, 27–35) expresses the opinion, based upon extensive investigation, that successful curing depends upon (1) non-development of acidity through avoidance of undue exposure to bacteria and yeasts ; (2) complete killing of the embryo by heat ; and (3) maintaining the oxidising enzymes in an uninjured condition. A product of superior colour and aroma is obtained by keeping the beans at a temperature of 40°–60° for several days out of contact with bacteria and yeasts. During fermentation a large proportion of the pulp is gradually transformed into a liquid (" sweatings "), which is allowed to drain away. When the beans are satisfactorily cleared of the pulp and have assumed the requisite aroma and colour they are removed to sieves or troughs and thoroughly washed with water if such a cleaning process be considered necessary. In order to improve the quality of the beans Defren (U.S.P. 1750795) suggests that they should be soaked in successive changes of water for a sufficient time to remove at least the greater proportion of the soluble bitter ingredients. As an alternative to the fermentation process, a method has been devised whereby the beans are treated with a 1% solution of sodium carbonate for 10 minutes at 45°. It is stated that cocoa prepared in this way is perfectly stable and sterilised, and contains no preformed sugar. Theobromine is not present in the free state but is formed, together with sugar and tannin, by hydrolysis. After cleaning by fermentation or other means the beans are dried to a moisture content of 5–8% by heating artificially or by subjection to the rays of the sun. Care should be taken to control the temperature, as above 50°C. the flavour is likely to be adversely affected. If more than 8% of moisture is allowed to remain, the beans may become mouldy. In order to hasten the drying finely powdered dried earth is sometimes spread over and intimately mixed with the beans. The mass is then raked, hand rubbed, or "danced" with the bare feet, the friction thus set up also polishing the beans, thus improving their appearance, and removing mildew, thereby eliminating the possibility of the growth of mould during subsequent storage.

Manufacture.—The preliminary processes of manufacture are :

(*a*) *Sifting* out of sand dust and small stones.
(*b*) *Picking* out by hand of the empty beans and foreign matter, such as larger stones, grass, and wood.
(*c*) *Roasting.*
(*d*) *Husking* by breaking up the beans and separating the husks.

Berhardt (Chem.-Ztg. 1889, **13**, 32) has found, from the results of actual factory working, that the losses in these operations amount to 2–3% in sifting, nearly 1% in picking, about 5% in roasting, and 12 or 13% in husking, making a total loss of over 20%. Machinery is now in use which combines the first and second operations with the sorting of the beans into various sizes. The objects of roasting are to develop to the full extent the characteristic aroma and flavour of the cocoa, to render the starch granules more soluble, to modify the tannin and other astringent ingredients, to render the husk brittle and easily removable, and to drive moisture from the nib, thus rendering it fit for the subsequent operations. The process, which requires considerable care and experience, is conducted in rotary cylinders heated to a temperature varying from 160 to 315°C. by coke fire, gas flames, or hot air or superheated steam in pipes lining the cylinders, Uniformity of roasting is facilitated by grading the beans so that they are approximately of the same size in an operation. Defren (Food Ind. 1930, **2**, 248), however, objects to this usual method of roasting alleging loss of flavour, charring, and difficulty of control. He suggests that the aromatic flavours are better retained by the use of a stream of heated air to reduce the moisture content to about 3%. The dampers should then be closed and roasting at about 100° continued. After roasting, the beans are cooled and then gently crushed in a "kibbling" mill to fracture the crisp husk and break down the kernel into its natural angular fragments or "nibs," after which the nibs, husks, and hard rod-shaped germs are separated by winnowing and sieving. Care must be taken that the process of cooling is not carried too far or the nibs will become brittle and break up into small particles which may be lost in the husk. The husks constitute, on an average, about 12 or 13% of the weight of the bean, varying from 7 or 8% in the thin-walled beans of Ceylon and Java to 18% in those of Trinidad and the West Indies, which have a much thicker shell. The nibs represent about 80% and the germ 1%. The remaining 6 or 7% is accounted for by loss. The husks form a low-priced product sometimes used, after grinding, in cheaper grades of cocoa and chocolate and occasionally, under the name of "cocoa tea" being infused as a beverage which has the flavour of weak cocoa. They are also used as fertilisers, and as an ingredient in cattle-feeding materials. They have also been suggested for use as cattle bedding, but Mach and Herrmann (Landw. Versuchs-Stat. 1933, **117**, 265) express the opinion that they are not suitable owing to their low water absorption capacity compared with that of straw, whilst, if the proportion of theobromine is over about 1%, their consumption by the animals would be dangerous.

The nibs constitute the important part of the bean and form the basis of all cocoa and chocolate preparations, their ultimate use governing the method of treatment to which they are subjected. This, however, does not apply to the first stage, in which the nibs are pulverised in a hot mill. They are fed through a hopper on to revolving stones encased in a jacket heated to about 45°C. Here the nibs are speedily reduced to a molten mass owing to the high content of low-melting fat (about 30°C.). When the mass is considered to be completely melted and homogeneous it is allowed to run into moulds where it cools and solidifies. It is then in a convenient form for storage, transport, or further treatment, and it is in this state that much cocoa forms an article of commerce under the title "block cocoa."

The form in which cocoa to be consumed as a beverage is prepared for sale is known commercially as "cocoa powder." The high proportion of fat in block cocoa would render it indigestible and prevent complete mixture with water. About 60 or 70% of the fat is therefore removed by subjecting the block cocoa to a pressure of about 1,200 or 1,400 lb. per sq. in. at a temperature of 70°–80°C. The cocoa butter flows out through a special orifice and is afterwards solidified in moulds ready for use in surgical and pharmaceutical preparations and in the manufacture of chocolate confectionery. Although in this process the fat or "cocoa butter" was at first regarded as a waste product, its commercial value is now so high as to form an inducement for its abstraction from the cocoa independently of the demand for the defatted cocoa. The cocoa mass, which after this treatment contains about 25% of fat, is then cooled, crushed in a mill, and sifted, the resultant powder being cocoa from which the beverage is prepared. A feature of the cocoa trade for many years has been the preparation and sale of so-called *soluble cocoas.* These may be prepared either by treatment of the cocoa powder with steam or ammonia or ammonium carbonate, or by admixture with alkali such as sodium or potassium carbonate. In the first case the cocoa tissue is softened and the fat rendered less liable to separate out. In the second case, when the mixture is treated with boiling water for the preparation of the beverage, an emulsion is formed which retains the powder in suspension. These admixtures are not regarded as adulteration, but if other substances are added the fact should be disclosed. Thus it is a common practice to offer for sale preparations in which starch or sugar or both have been added to the cocoa powder. The designation of these by some such term as "chocolate powder" is generally considered to be adequate indication of the presence of substances other than cocoa. The addition of starch or sugar, if properly disclosed, is not to be condemned. Indeed, it may well be claimed that the presence of the starch is of dietetic advantage, increasing the carbohydrate content and rendering the mixture more easily assimilated by those who find the pure cocoa product, with its high fat content, indigestible. (For preparations of cocoa, *see* Chocolate.)

Composition of Roasted Nib.—This has been the subject of considerable investigation, and Whymper ("Cocoa and Chocolate—Their Chemistry and Manufacture," London, 1912) gives the following as typical results:

	1.	2.	3.	4.	5.	6.
Moisture	5·23	6·3–8·5	3·7–4·4	3·00	5·86	3·11
Fat	50·44	46·9–52·1	45·3–54·4	50·00	50·30	54·37
Albuminoids	13·26	11·6–21·1	7·4–13·0	—	—	—
Cellulose	6·40	3·3–6·6	—	—	4·05	—
Ash	2·75	2·9–4·8	2·4–3·9	3·07	3·87	3·41
Gum	2·17	—	—	—	—	—
Alkaloids	0·84	0·3–0·5	—	—	—	—
Cacao red	2·20	—	—	—	—	—
Pentosans.	—	—	—	—	1·36	—
Nitrogen	—	—	—	2·50	—	—
Fibre	—	—	—	2·80	—	—
Astringent matter . .	6·71	7·2–8·6		—	—	—
Cane sugar	—		26·3–39·4	—	—	—
Starch	4·20	8·7–12·6		—	9·97	—
Cold water extract . .	—	—	—	11·60	—	9·67

[1] J. Bell, "The Chemistry of Foods," 1887, p. 76.
[2] Zipperer, "Untersuch. über Kacaoets," pp. 56, 57
[3] Heisch, Analyst, 1875, **1**, 142.
[4] N. P. Booth, Analyst, 1909, **34**, 144.
[5] R. Adan, Internat. Cong. App. Chem. VIIIC, 203.
[6] F. Bordas, Internat. Cong App. Chem. VIIIC, 188.

Cocoa Butter.—The most important ingredient of the cocoa bean is the fat which, as already indicated, is, in itself, a valuable commercial commodity sold under the names "Cocoa Butter" or "Cacao Butter." Its principal uses are for medical purposes and for addition to block cocoa in the manufacture of chocolate confectionery. Under the title "Oleum Theobromatis" the "British Pharmacopœia" describes cocoa butter as "the solid fat expressed from the roasted seeds of *Theobroma Cacao.* A yellowish-white solid fat; odour slight, agreeable and resembling that of cocoa; taste bland and characteristic. Somewhat brittle but softens at 25°C." Cocoa butter is readily soluble in ether, chloroform, turpentine, and boiling alcohol from which it crystallises out almost completely on cooling. Lewkowitsch (J.S.C.I. 1933, **52**, 236) gives the following as its approximate composition: α-palmitooleostearin 55%, oleodistearin 25%, β-palmitodiolein about 20%. Lüning and Drude (Z. Unters. Lebensm. 1931, **61**, 491) tested several samples by Graf's method of fractional precipitation of the magnesium salts (Arch. Pharm. 1888, **226**, 843) with the modification that the magnesium salts were dried at 95° till of constant weight. They also determined the melting-points of the fatty acids and concluded that no acids higher than stearic were present.

The following are some of the values of cocoa butter as published by various investigators:

	1.	2.	3.	4.
Specific gravity . .	0·990–0·998 (15°C.)	0·964–0·974 (15°C.)	0·8823–0·8829 (60°C.) 0·8572–0·8581 (90°C.)	0·8831(60°C.) 0·8562(99·9°C.)
Saponification value .	192–198	192–195	—	—
Iodine value . . .	34–40	32–42	34·9–40·1	—
Refraction $[n]_D^{40}$ . .	1·4565–1·4570	—	1·4568–1·4570	—
Melting-point °C. . .	32–34	30–34	30·2–31·2	32·6
Redwood Viscosity at 60°C.	—	—	99·1–101·3	102

[1] Elsdon, "Edible Oils and Fats."
[2] Whymper, "Cocoa and Chocolate."
[3] Tate and Pooley, Analyst, 1921, **46**, 229.
[4] Knapp, Moss, and Melley, Analyst, 1927, **52**,

The differences, if any, between fat obtained from cocoa by the ordinary commercial method of expressing and that obtained by the method of extraction with a solvent as often followed in the laboratory may be of importance, particularly when considering the possibility of the presence of some foreign fat. Visser (Chem. Weekblad, 1932, **29**, 40) considers that the term " cacao butter " without further designation should be applied only to the fat obtained by expression. Fincke (Bull. Off. Intern. Fabr. Choc. Cacao, 1932, **2**, 327) states that when fat is extracted from chocolate for examination, ether and not light petroleum should be the solvent, as the latter will not dissolve out the wax which is likely to be present in the adulterant fat. Castiglioni (Ann. Falsif. 1935, **28**, 24) gives two methods of differentiation between extracted and expressed cocoa fat. In the first the melted fat is shaken with glacial acetic acid and allowed to stand. The fat on rising to the top is then examined by ultra-violet light and if extracted shows a bright yellowish-green fluorescence. In the second the fat is heated with alcohol, hydrochloric acid and antipyrine, when a pink colour indicates that the fat has been extracted. Neither reaction is given by fats commonly used as adulterants. Kaufmann (Chem. Umschau. Fette, Oele, Wachse, Harze, 1931, **38**, 265) found that whilst the refractometer readings showed no marked difference the Haber-Löwe interferometer gave differences as high as 80 on an arbitrary scale.

Although, in the preparation of cocoa as a beverage, the removal of a considerable portion of the fat is desirable, the high commercial value of cocoa butter, compared with that of the raw bean or the various preparations of cocoa, has promoted the removal of the fat from the nib to an excessive degree and its replacement in chocolate confectionery by other fats of vegetable origin. In addition to the economic reason for the extraction of the fat it is sometimes claimed that, for certain purposes, the admixture of a foreign fat is advantageous, facilitating manufacture and providing a more stable product. The two fats most commonly used for this purpose are coconut or palm kernel stearin and the so-called " illipé butter," a name given in the chocolate trade to Borneo tallow. Recently hardened coconut, palm kernel, peanut, and cottonseed oils have been used. The hardened oils have the advantages of more uniform composition, better control of the melting-point and elimination of "sugar bloom." Williams (Chem. Trade J. 1935, **95**, 4) states that peanut and cottonseed oils hardened to 35° have a greater degree of contraction on cooling to 10°–12° than either palm kernel or coconut, probably because of the higher proportion of unsaturated glycerides in the former. Coconut oil when used is readily detected by the various constants. Thus :

	Sp.gr. 15·5°C.	Saponification value.	Iodine value.	M.p. °C.	Refraction, $[n]_D^{40}$	Kirschner. value	Titre (f.p. of fatty acids, °C.)
Cocoa butter (Elsdon) . .	0·990–0·998	192–198	34–40	32–34	1·4565–1·4570	0·5	49–50
Coconut oil—							
Fryer and Weston . .	0·926	255–260	8–9	23–26	—	—	21–25
Bolton	—	255–258	7·9–8·8	23–26	1·4486–1·4492	1·6–1·9	—

Illipé butter, however, does not display any such marked differences from cocoa butter. Tate and Pooley (*l.c.*) determined the following values :

	Sp.gr. 60°C.	Redwood Viscosity at 60°C.	M.p. °C.	Iodine value.	M.p. of fatty acids.	Refraction, $[n]_D^{40}$
Cocoa butter . . .	0·8823–0·8829	99·0–101·3	30·2–31·2	34·9–40·1	47·7°–49·2°	1·4568–1·4570
Illipé butter . . .	0·8823–0·8840	100·7–105·7	30·3–35·8	27·4–33·4	52·1°–54·1°	1·4561–1·4573

It will be seen that the respective values for the two fats are so close that none affords by itself an effective means of differentiation. Tate and Pooley proposed to multiply together certain of the constants determined in a standard manner, thus obtaining a composite factor for each of the fats. The constants treated in this way were the specific gravity at 60°C., the sp.gr. at 99°C., the viscosity, the melting-point, the melting-point of the free fatty acids, and the reciprocal of the iodine value. The composite factors thus obtained on twelve samples of cocoa butter varied from 2,839 to 3,347, average 3,150. Those obtained for a similar number of samples of illipé butter ranged from 3,890 to 4,771, average 4,403. Knapp, Moss, and Melley (Analyst, 1927, **52**, 452) consider this method useful if applied with discretion, but they suggest that each worker should determine his own average constants. They further suggest the use of the " titre " value, particularly if other substitutes are suspected. They also consider the " titre " value the most useful single factor which can be determined. That for cocoa butter varies only between 49°C. and 50°C., whilst the mean value for Borneo tallow is

54·6°C., and they are of opinion that a sample of reputed cocoa butter is adulterated if it gives a "titre" over 50°C. A method proposed by Bywaters, Maggs and Pool (*ibid.* 1927, **52,** 324) takes advantage of the extreme supercooling to which cocoa butter can be subjected. It is based upon the "turbidity temperature" of the melted fat. The method appears to afford a valuable approximation to the percentage of illipé butter present. Pichard (Compt. rend. 1923, **176,** 1224) also uses the minimum temperature of supercooling as a means of detection of adulteration. By plotting the temperature of a fused fat as a function of time, cocoa butter from different sources gave the same curve, differing from those for all possible adulterants. The method suggested by Koehler (*ibid.* 1924, **178,** 940) is based upon a comparison, preferably at 15–20°, of the number of drops of ethyl acetoacetate which must be added to a 20% solution in chloroform of the sample to obtain constant turbidity unchanged by the addition of another drop. The "turbidity number" varies considerably with temperature, and the sample and pure cocoa butter should be treated simultaneously under identical conditions. Hanuš and Komorousová (Chem. Listy, 1925, **19,** 394) define the "ethyl ester number" as the number of c.c. of *N*/10 potash necessary to saponify the ethyl ester in the distillate obtained from 5 g. of fat after conversion of the glycerides into ethyl esters. The "numbers" for coconut oil and cocoa butter are given as 23 and 3 respectively, referred to 1 g. of fat. Ashmore (Analyst, 1934, **59,** 515) has brought forward an ingenious apparatus for observing the temperature at which molten cocoa butter crystallises. A beam of light led by internal reflection along a glass rod is projected through a small tube of the molten fat suitably housed in a darkened chamber. The appearance of the tube is noted during cooling. As soon as crystals of solid glyceride separate the tube is at once illumined by the Tyndal effect produced. The temperature at which this occurs can be noted with considerable precision and may be used for detecting the presence of certain adulterants. Thus genuine cocoa butter has a crystallising temperature of 20°C., whilst a temperature of 31·2° was recorded for Borneo tallow.

The variation in the melting-point of cocoa butter and adulterant fats due to varying time and conditions of crystallisation has been recognised by many workers. Fincke (Z. angew. Chem. 1925, **38,** 572) recommends that the fat should be cooled slowly and with stirring. He found that for cocoa butter the temperature after 0·66, 2·5, and 14 days respectively was 32·3°, 32·3°, and 32·6°. Sabalitschka (*ibid.* 1925, **38,** 1013) considers that, in order to obtain complete solidification, it is necessary to leave the melting-point tube on ice for several weeks before making the determination. In order to overcome the difficulty Tate and Pooley (*l.c.*) determined the melting-point by placing a shaving of fat upon mercury contained in a porcelain crucible in which the thermometer was suspended with the bulb fully immersed. The crucible was placed on a wire gauze over a very small flame and the temperature taken when the first signs of transparency were observed in the shaving.

THEOBROMINE (*v.* CAFFEINE AND THE ALKALOIDS OF TEA, COFFEE AND COCOA) is the principal alkaloid in cocoa and is closely related to caffeine which is also present to a small extent in cocoa. The proportion in which theobromine has been found to be present has varied considerably, probably in consequence not only of variations in the different type of bean but also, in some measure, of the different methods of estimation employed. The caffeine is usually included with the theobromine, from which, however, it can readily be separated by means of cold benzene in which caffeine is soluble but theobromine practically insoluble. According to Kreutz (Z. Nahr. Genussm. 1909, **17,** 526) the proportions found have often represented only the *free* theobromine. He maintains that part of the alkaloid is combined and is not extracted until the cocoa has been subjected to hydrolysis. He found proportions varying from 2·8 to 5·1%. Wadsworth (Analyst, 1921, **46,** 32) suggests a method of determination in which 10 g. of the fat-free material are triturated in a small porcelain dish with magnesium oxide and water, the mass is then refluxed with tetrachlorethane and, after filtering, the residue is again refluxed with the same solvent and the united washings distilled to small bulk. Precipitation is then effected with ether and the precipitate dried and weighed. Wadsworth further states (Analyst 1922, **47,** 152) that the theobromine content varies with the type of bean from 2·2 to 3·8% on the dry fat-free residue. Goryainowa (Khem. Farm. Prom. 1932, **6,** 227) suggests a method embodying some slight modifications of that proposed by Wadsworth. During the process of fermentation the theobromine content of the nib decreases, whilst that of the shell increases. According to Churchman (J.S.C.I. 1926, **45,** 149) the percentage in cocoa shell varies from 0·2 to 3%.

ALBUMINOIDS.—These have been but little studied, but Stutzer (Z. angew. Chem. 1891, **4,** 368) has classified the nitrogenous ingredients of cocoa as follows:

(1) Non-proteids, substances soluble in neutral water solution in presence of copper hydroxide (theobromine, ammonia, and amino compounds).

(2) Digestible albumen, insoluble in neutral water solution in presence of copper hydroxide, but soluble when treated successively with gastric juice and alkaline pancreas extract.

(3) Insoluble and indigestible nitrogenous compounds.

According to Stutzer's analyses, the proportion of albuminoids in cocoa powder manufactured without chemicals is between 17 and 18%, of which 10% is soluble or digestible albumen, the remainder (over 40% of the whole) consisting of insoluble and indigestible substances. Forster (Hyg. Rundschau, 1900, 314), however, maintains that the proportion of digestible albuminoids reaches as high as 80%, his experiments being made on the human subject, whilst Stutzer's were conducted under laboratory conditions.

STARCH, as in oleaginous seeds generally, is not very abundant. Owing, however, to the occasional necessity to identify and estimate foreign starch in cocoa preparations its character and proportion in the bean are important. The starch grains are nearly spherical with a very indistinct nucleus. They have a tendency to unite in small groups of 3 or 4 and rapidly lose the colour imparted by iodine. The average size is about 0·005 mm. The proportion in which it occurs in the nib has been variously estimated as from 2 to 20%, but many of the results are too high, owing, no doubt, to the conversion of cellulose into sugar when the acid method for the starch conversion is employed. The diastase method is preferable in the presence of cellulose. The average amount of starch is from 4 to 5%, or about 8% calculated on the fat-free bean.

TANNIN AND COLOURING MATTER.—It has long been known that the raw bean, which is nearly white, contains an astringent principle resembling tannin which is rapidly oxidised to form " cocoa red," thus imparting to cocoa its characteristic colour. Bell states that this astringent substance is different from the tannin of tea and coffee, and that its rapid change to cocoa red, even during the process of analysis, renders its quantitative estimation difficult. Adam (Analyst, 1928, **53**, 369) found that the unfermented cocoa bean contains (*a*) a substance belonging to the catechin series, (*b*) a catechu tannin, and (*c*) a compound of cocoa tannin and caffeine. The colouring matter which is subsequently developed consists of cocoa red and cocoa brown, which are complex alteration products of the catechin and tannin originally present. The cocoa catechin undergoes alteration during the process of fermentation and is absent from the completely fermented bean. Fincke (Z. Unters. Lebensm. 1928, **55**, 559) states that both the cocoa red and the cocoa brown are tannin substances, the former occurring in variable amount in the fresh seeds, whilst the latter is gradually produced during fermentation, roasting and grinding. Steinmann (Z. Unters. Lebensm. 1933, **65**, 454), on the other hand, states that the formation of cocoa red in the bean depends mainly upon the type of cocoa; white unfermented beans contain no cocoa red which is found only in beans with violet cotyledons. Unfermented beans dried in the dark contain no cocoa red, but those subjected to the action of light contain free cocoa red which, however, disappears on fermentation. The increase in colour intensity on long fermentation is ascribed to the liberation of combined cocoa red, induced by the acids, chiefly acetic, formed during fermentation. This cocoa red goes over slowly into cocoa brown. The development of the dark brown-red colour in the shell of the bean on drying is probably a photochemical reaction. Steinmann further states that whilst cocoa red is easily soluble in alcohol, cocoa brown will dissolve only with difficulty, but does so readily in an aqueous alkaline solution giving a deep brown colour. On hydrolysis cocoa red decomposes into glucose, tannin and a resinous substance.

MINERAL MATTER.—The ash in cocoa nibs varies from 2·4 to 4·5%, the average according to Zipperer being 3·6% in raw and 3·9% in the roasted kernels. Approximately half the ash (which is rich in potash and phosphates) is soluble in water. The ash is naturally lower than the average when starch or sugar has been added, and higher when fat has been abstracted or when the cocoa has been adulterated with husks or coloured with pigments. A high alkalinity in the ash of cocoa powders indicates treatment with alkali as described in the preparation of " soluble " cocoa (*see* von Fellenberg, Mitt. Lebensm. Hyg. 1932, **23**, 29).

COCOA SHELL.—The chemical detection and approximate determination of shell used in cocoa products is of use only in cases of gross adulteration. Microscopic methods are generally admitted to be more suitable. In this connection von Fellenberg (*ibid.* 1921, **12**, 301) found that a sample of cocoa powder contained stone cells 3–6 times the diameter of the cells characteristic of cocoa shell and resembling those of walnuts. These show mostly a thick wall in the interior of which are elongated pores. Sometimes no thick wall is noticeable, in which case the pores reach the periphery. They are noticed in many cocoas rich in shell. They are characteristic of the cocoa fruit shell and samples showing them contain shell of the fruit as well as that of the seed. Their presence may therefore be taken as a certain indication of adulteration with added shell. Koperberg (Chem. Weekblad, 1926, **23**, 646) suggests that the stone cells in the defatted material should be counted and compared with standards containing a known percentage of shell. He expresses the opinion, however, that the result can be regarded only as an approximation, as commercial samples are not sufficiently uniform. Griebel and Sonntag (Z. Unters. Lebensm. 1926, **51**, 185) agree with this but suggest that it may be possible to set limiting figures for each cocoa product based upon this method. Alpers (*ibid.* 1927, **54**, 462) further draws attention to the fact that stone cells in cocoa products are deformed and broken up by grinding and regard should be had to this fact when comparing samples with standards. Plücker and Steinruck (*ibid.* 1931, **62**, 364) suggest a method for cleaning the tissue, colouring with safranine and counting the cells. Winkler (J. Assoc. Off. Agric. Chem. 1935, **18**, 427) states that crude cellulose is the most promising characteristic for indicating the proportion of shell in cocoa products, the spread in percentage of this constituent in nib and shell being much greater than that of crude fibre. The ash of shells differs from that of nib, being 2–3 times as great, and being richer in alkaline carbonates and silica.

COCOA FEEDING MEAL.—The use of the products of the cocoa bean in the preparation of feeding stuffs for animals renders important the findings of investigators who have expressed opinions adverse to such use. Rothéa (Bull. Sci. Pharmacol. 1920, **27**, 355) gives, as a reason for the unsuitability of cocoa shell as a horse food, the high percentage of theobromine, of which he found 1·09%. He is of the opinion that untreated cocoa shell is unfit for animal food. Marchadier and Goujon (Le Mans, J. Pharm. Chim. 1919, **20**, 209) state that cocoa shell deprived of its extractive matter is devoid of nutritive value, and its sale as food for animals should be prohibited. They agree with Rothéa, however, in suggesting that the alkaloidal bases of cocoa shell are dangerously toxic, and that the shell should be used only in small daily doses. With regard to cows, Bunger and Lamprecht (Milch. Zentr. 1926, **55**, 49) find a decided increase in total protein of the milk when cocoa meal is fed, the casein increasing more than the albumin. Lactose, on the other hand, decreases somewhat. Aplin and Ellenberger (Vermont Agric. Exp. Sta. Bull. 1927, **272**) found that cocoa meal in the rations of milking cows increased the proportion of fat but reduced the milk yield so that the gain in fat production was small. They further state that the theobromine was responsible for these changes, the caffeine content producing no noticeable effect. Aplin (*ibid.* 1927, **271**) also states that cocoa meal is not a suitable ingredient of hog or pig ration, causing litters of undersized pigs when fed to pregnant sows and exerting a toxic effect on young pigs. Robinson (Ohio Agric. Exp. Sta. Special Circular, 1932, 26) states that cocoa bean is not of great value in fattening hogs, and attributes the poor results to the presence of theobromine and caffeine.

F. G. H. T.

COCONUT, COCOANUT. The fruit of the cocoanut palm, *Cocus nucifera* L. The fibrous outer husk of the cocoanut yields the coir fibre largely used in the manufacture of matting and cordage. The dried fleshy endosperm of the nut is the copra of commerce, or when specially cleaned, dried, and shredded forms the "desiccated cocoanut" or "cokernut" used in confectionery. The press-cake from oil extraction, known as "cocoanut cake," is a much valued cattle food.

Of the whole nut 30–50% consists of husk; the remainder, the cocoanut usually met with, comprises shell 27–28%, fleshy kernel 55–56%, "milk" 17–18%.

The following are average analyses of cocoanut products:

	Milk.[1]	Kernel.	Desiccated cocoanut.	Cocoanut cake.	Copra.
Water . .	91·5	46·3	3·5	10·7	5·8
Protein . .	0·4	4·1	6·3	19·1	8·9
Fat . . .	1·5	37·3	57·4	11·1	67·0
Carbohydrate	4·6	7·9	31·5	41·0	12·4
Fibre . .	0·0	3·4		14·1	4·1
Ash . . .	0·8	1·0	1·3	4·0	1·8

[1] From ripe nuts.

The protein of cocoanut flesh consists almost entirely of a globulin, conglutin (Ritthausen) or phytovitellin (Chittenden and Setchell) containing 17·8–18·4% N and 1·8% ash. A small amount of a proteose is also present. Johns, Finks and Gersdorff (J. Biol. Chem. 1919, **37**, 149, also Jones and Johns, *ibid.* 1920, **44**, 283, 291) record the nitrogen distribution of the globulin as:

	% of total N.
Amide-N	7·99
Humin-N	1·5
Cystine-N	0·96
Arginine-N	29·5
Histidine-N	3·68
Lysine-N	6·41
Amino-N of filtrate . .	45·44
Non-amino-N of filtrate .	4·6

The composition of the products of hydrolysis is:

	%
Alanine	4·11
Valine	3·57
Leucine	5·96
Serine	1·76
Cystine	1·44
Aspartic acid	5·12
Glutamic acid	19·1
Tyrosine	3·18
Phenylalanine	2·05
Proline	5·54
Tryptophan . . .	present
Arginine	15·92
Lysine	5·80
Histidine	2·42
Leucylvaline anhydride .	0·64
Ammonia	1·57

The milk of the cocoanut consists of an emulsion of oil in water stabilised by protein, the colloidally dispersed proteins being adsorbed at the oil-water interface. The aqueous phase contains dissolved sugar (Clemente and Villacorte, Univ. Philippines Nat. Appl. Sci. Bull. 1933, **3**, 7). In the milk of young nuts sucrose is the principal sugar, and small amounts of glucose and mannitol are reported. The proportion of glucose and sucrose appears to vary considerably in the different stages of maturation (Dunstan, Trop. Agric. Mag. Ceylon Agric. Soc. 1906, **26**, 377; Lahille, Bull. Econ. Indochine, 1920, **23**, 1). According to Gonzalez y Sioco (Philippine Agric. Forest, 1914, **3**, 25) the ripening is characterised by three stages: (1) commencement of endosperm formation when invert sugar and amino-acids accumulate in the milk, (2) drying out of tissue of green nut when sucrose is produced, (3) oil formation in the endosperm during which the total solids of the milk diminish. In dried copra meal, Caray (Philippine Agric. 1924, **13**, 229) found the following percentages of carbohydrate materials: sucrose 14·3, raffinose 2·4, galactose 2·4, pentoses 2·4, fructose 1·2, glucose 1·2, cellulose 15·5, pentosans 2·2, starch 0·9, dextrin 0·6, galactan 0·5.

Buchofen records the following mineral analyses:

	Husk.	Shell.	Kernel.	Milk.
Total ash	1·63	0·29	0·79	0·38
K_2O . .	30·71	45·01	54·06	34·57
Na_2O .	27·56	23·67	2·66	13·96
CaO . .	4·14	6·26	3·10	7·43
MgO . .	2·19	1·32	1·98	3·97
Fe_2O_3 .	0·54	1·39	0·59	trace
P_2O_5 .	1·92	4·64	20·33	5·68
SO_3 . .	3·13	5·75	8·79	3·94
SiO_2 . .	8·22	4·64	1·31	2·95
Cl . .	27·88	9·44	9·25	35·52

Small proportions of zinc occur in the endosperm but not in the milk (Bertrand and Benzon, Bull. Soc. Sci. Hyg. aliment, 1928, **16**, 457).

A. G. Po.

COCONUT OIL GROUP. Under this heading is grouped a number of closely similar fats (often known as the "nut oils," or in German as "Leimfette"), which are derived from the seeds of various tropical species of the family *Palmæ*, and which differ from other vegetable fats by having high saponification values (235–265) in conjunction with high Reichert-Meissl values (5–9) and Polenske values (10–20): the iodine values are fairly low (*c.* 8–25). The fairly high Reichert-Meissl values, consequent upon the presence of the soluble volatile fatty acids, caproic and caprylic acids, bring these fats into superficial relationship with the mammalian milk fats; they differ essentially from the latter, however, not only in containing vegetable phytosterols (in the unsaponifiable fraction) in place of the cholesterol of the animal fats, but also in that the nut oils do not contain any butyric acid. The presence of the volatile caprylic and capric acids differentiate the nut oils from other fats (such as those of the Dika Fat Group, *q.v.*, and Laurel Fat Group), which likewise possess high saponification values but do not contain appreciable amounts of acids of lower molecular weight than lauric acid, and hence display very low Reichert-Meissl and Polenske values.

Two fats of this group, *viz.* coconut oil and palm-kernel oil, are of very great commercial importance, whilst the trade in babassu nuts and murumuru nuts, which has become established within the last twenty years, seems likely to increase. A number of nuts of this group, such as cohune nuts (from *Orbignya cohune* Mart. Dahlgren, *v. infra*), mocaya, Paraguay or gru-gru palm nuts (from *Acrocomia sclerocarpa* Mart.), tucum and aouara nuts (from *Astrocaryum tucuma* Mart. and *Astrocaryum vulgare* Mart. (*cf.* Bray and Elliott, Analyst, 1916, **41**, 298; Bolton and Hewer, *ibid.* 1917, **42**, 35; Freise, Chem. Umschau, 1931, **38**, 216), and the nuts of the kokerite or inaja palm, *Maximiliana regia* Mart. (*cf.* Bull. Imp. Inst. 1916, **14**, 8; 1927, **25**, 1) occasionally appear on the market as sources of coconut-like fats. *Cocos bonetti*, Becc. is being cultivated experimentally at Suchum in the Black Sea region; as might be expected, the oil from this species, which grows on the northern limit of distribution of the genus *Cocos*, has a higher iodine value (*viz.* 23–24) than the fats from the tropical members of the group, and it is therefore proposed to hydrogenate the oil, in order to render it more acceptable as a substitute for coconut oil (*cf.* S. Ivanov and Alissova, Chem. Umschau, 1929, **36**, 401). The fats from a number of other species, such as the burity and murity palms (*Mauritia* sp.), the jauary palm (*Astrocaryum jauary* Mart.), the piririma palm (*Cocos syagrus* Drude), and other species of *Attalea*, *Maximiliana*, etc., are utilized by the natives of the countries in which they grow for edible purposes, as burning oils, or in pharmacy or soap-making; it is possible, also, that such fats may be included at times in the "coconut oil" prepared in such districts.

It may be pointed out that the fats discussed in this article are all derived from the *seeds* (kernels) of the palms; in some instances, for example, in the case of the common oil palm *Elaeis guineensis*, and the aouara palm, the pericarp or fruit-flesh surrounding the seed is also rich in oil, which differs, however, considerably from the corresponding seed-fat; these *palm-fruit* fats will be discussed under the heading PALM OIL.

Coconut Oil is the fat derived from the kernels of the coconut palm, *Cocos nucifera* L., which grows on all coasts and islands in the tropics. The tree is supposed by De Candolle (*cf.* A. W. Hill, Nature, 1929, **124**, 133, 151) to have been indigenous to the Malayan Archipelago, whence the seeds, well protected by the enveloping thick coir, were carried by sea-currents eastward to the Pacific Islands and the coast of Central America, and to the west to Ceylon and Africa, so that it is now found growing wild, or under semi-cultivation, on all tropical coasts in both hemispheres; it is, however, especially abundant on the Malabar and Coromandel coasts of India, in Ceylon, and in the East Indian and Pacific Islands. Apart from self-planted or "wild" coconut land, the extent of which cannot be calculated, it has been estimated (1930–1932) that about 7¼ million acres are devoted to the cultivation of the coconut, of which some 96–97% lie in Asia and Oceania, and about 53% within the British Empire. Whilst the Indian acreage of some 1,330,000 acres is the largest area in any single country, the whole of the crop is now consumed locally, leaving no balance for export, and the chief countries exporting copra or coconut oil, or both, are the Philippine Islands, the Dutch East Indies, the South Sea Islands, Ceylon, and Malaya. (Within the last few years the proportion of the Cingalese exports destined for India has rapidly increased and amounted to 95% of the total shipments from Ceylon in 1936). The total world shipments of copra and coconut oil (calculated as copra containing 65% of oil) from the principal exporting countries are of the order of 1⅓ to 1½ million tons per annum, of which, from 1924–1930,[1] 35% (on the average) was furnished by the British Empire (including Ceylon), and about 30% each by the Philippine Islands and Dutch East Indies. These shipments represent about 57% of the total production, the balance of 43% being consumed locally by the copra-producing countries. (For detailed studies of the statistical and economic position of coconut oil and copra, from which the above figures have been extracted, *see* "Survey of Oilseeds and Vegetable Oils," No. 2; "Coconut Palm Products," Empire Marketing Board, E.M.B. 61, Dec. 1932, H.M.S.O.; "Vegetable Oils and Oilseeds," Imperial Economic Committee, 1936, H.M.S.O.;

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[1] Full figures for later years have not been published in collated form, but it may be estimated from the available data (*cf.* "Vegetable Oils and Oilseeds," Imperial Economic Comm., 1936) that for 1933–1935 the proportions are about 30–33%, 33–35%, and 27–33% for the British Empire, Philippine Islands, and Dutch East Indies respectively.

Snodgrass, "Copra and Coconut Oil," Leland-Stanford Univ., 1928).

The coconut industry in Ceylon and Malaya is described by F. C. Cooke (Dept. Agric. S.S. and F.M.S. Gen. Ser. 1932, No. 8), who also makes a comparative report on the Philippine Islands industry in a later publication (*ibid.* 1936, No. 23; *cf.* Gothwaite, "Trade in Philippine Copra and Coconut Oil," U.S. Dept. Commerce, Trade Promot. Ser. No. 11, 1925; Snodgrass, *l.c.*).

The coconut palm flowers when about 5–7 years old, and begins to bear fruit from the age of about 8 years up to 30 or 60 years or more, according to the variety of the plant and cultural conditions. The large, drupaceous fruit consists of an outer skin and thick fibrous pericarp (from which the well-known "coir" is obtained) surrounding the stone or "nut," which consists of a hard woody shell (endocarp) within which is the coconut kernel or seed. The fleshy endosperm or "meat" which contains the fat is built up gradually from a milky juice as the fruit ripens. When the nut is mature, the milky juice has almost disappeared, and the endosperm forms the well-known hollow kernel, in which the remainder of the juice (the coconut "milk") is enclosed. The fresh "meat" contains from 30–40% of fat and 50% of moisture.

Since the earliest times in the history of man, coconut kernels have been used as articles of food by the natives of the South Sea Islands and of India: the oil first became known in Europe in the eighteenth century, but neither the oil nor copra was imported in any notable quantities until 1820 (*cf.* Soames, B.P. 5842, 1829). In the United States, which is now the largest consumer of coconut oil outside the copra-producing areas (apparent consumption, *c.* 260,000 to 330,000 tons per annum), the utilization of coconut oil in soap-making only dates from the beginning of this century, whilst its employment in the manufacture of margarine has only developed since the World War.

France now follows the United States as the second largest non-tropical consumer of the oil (*c.* 120,000 tons per annum), whilst Germany, which was by far the biggest consumer in pre-War days and held second place from 1924 to 1929, fell to third place in 1930, and was just superseded in apparent consumption by the United Kingdom with 92,000 tons in 1931.

The most primitive native method of obtaining the oil consisted in merely chopping up the kernels and exposing the pieces to the sun until the oil exuded and could be collected. In India, where at an early date the oil was extensively used for food and in pharmacy, more refined methods, which form the basis of present-day commercial practice, were employed.

After removing the fibre the nuts were split, the "milk" poured off, and the half-nuts exposed to the sun until the kernels were dried and could easily be detached from the shells; the dried kernels were then triturated and expressed in order to recover the oil. The residual mass ("coconut poonac") was used as a cattle-food. The best quality of oil—the original "Cochin oil" from the Malabar coast—was prepared by throwing the pounded, dried kernels into boiling water and skimming off the liberated oil. The reputation of Cochin oil was such that the term has come to be used to designate the finest, whitest grades of oil, regardless of the place of origin or of the method employed to prepare the oil (as stated above, Indian-produced oil (and copra) is no longer exported to Europe). "Ceylon oil" was prepared in Ceylon by similar methods, but, owing to various circumstances, represented as a rule a slightly inferior grade of oil having a somewhat higher content of free fatty acid than the Malabar product.

A further expansion in the coconut industry followed when it was recognized that, whereas the fresh, moist kernels readily putrefy, causing hydrolysis and rancidification of the oil, well-dried kernels (containing less than 8% of water) could be preserved for a considerable time without damage to the contained oil, so that the drying treatment developed into a manufacturing process for producing the dried kernel —*copra*—for export to Europe and the United States, where the oil could be expressed on the large scale with modern machinery. Formerly, apart from the Cochin and Ceylon oils (amounting to about 10% of the total), all the industrial coconut oil ("copra oil") was thus prepared in the consuming countries from imported copra, and it is still true to-day that copra bulks far larger in the exports from the producing areas than does coconut oil. There has been a growing tendency, however, within recent years to establish modern oil mills in the principal copra-producing districts, such as the Philippine Islands, Ceylon, Dutch East Indies, and Malaya, and to export the oil as such, so that in the period 1927–1930 about one-quarter of the aggregate exports of copra and coconut oil from the copra-producing areas was shipped in the form of oil (E.M.B. 61, *l.c.*). Formerly a sharp distinction existed between "sun-dried" copra and "kiln-dried" or "smoke-dried" copra; for a given type of coconut, a "sun-dried" product, prepared by exposing the split nuts to the sun for several days, is the better, since it yields a paler and less acid oil; but in regions where the climate does not permit of this process, recourse must be had to artificial drying, and the split nuts are "kiln-dried" or "smoke-dried" by spreading them on (bamboo) grids supported over a fire of coconut shells and husks (*cf.* F. C. Cooke, *l.c.*, also Malay. Agric. J. 1936, **24**, 167, 332; 1937, **25**, 93). Even in Ceylon (which produces the highest-priced copra) it is now the usual practice to allow only a preliminary drying in the sun (for 1–2 days) and to complete the drying in the hot kilns (4–6 days); hence the term "sun-dried" has come to lose its original narrow significance, and is used in the trade as a designation of quality in copra, without especial reference to the mode of drying. In the somewhat primitive kilns employed, the fumes from the fire obtain ready access to the copra itself and impart to it a peculiar empyreumatic odour and also cause a certain amount of discoloration, and, occasionally, scorching; the quality of the product (which is judged by the appearance of the copra and by the colour, etc., of the oil obtain-

TABLE I.

USUAL ANALYTICAL CHARACTERISTICS OF FATS OF THE COCONUT OIL GROUP.

	Coconut oil.[1]	Palm-kernel oil.[2]	Cohune nut oil.	Babassu fat.	Murumuru fat.
Melting-point . . .	23°–28°C. (≯30°C.)	23°–30°C. (≯30°C.)	18°–20°C.	22°–26°C.	32°–35°C.
Specific gravity . .	*c.* $0{\cdot}874/^{99}_{15}$	*c.* $0{\cdot}873/^{100}_{15}$	$0{\cdot}868–0{\cdot}871/^{100}_{15{\cdot}5}$	*c.* $0{\cdot}867/^{100}_{15}$	—
Iodine value . . .	8–10 (7·5–9·5)	15–23[3] (14–19)	9–14	8–17	11–13
Saponification value .	250–264 (≮255)	243–250 (242–252)	251–256	246–263	237–242
Reichert-Meissl value .	6–8	5–7·5	6·8–8·5	5–9	*c.* 3
Polenske value . .	15–20	10–12	12·5–15·5	4–13·3 (usually 11–13)	*c.* 7
Bertram A-value . .	27·4–30·5	16·5–17(*a*)	—	19·5, 24·1 (*b*)	8·7 (*c*)
Bertram B-value . .	2·5–3·1	1·8–2·1(*a*)	—	1·9–2·0 (*b*)	1·4 (*c*)
Hehner value (insoluble fatty acids) . . .	88–91%	*c.* 90%		88–91%	*c.* 93%
Unsaponifiable matter.	*c.* 0·2% (≯0·8%)	0·2–0·8%	0·5%	0·3–0·8%	0·3–0·6%
Titre (f.p. of fatty acids)	20°–23°C.	20°–25°C.	*c.* 21°C.	21°–24°C.	*c.* 26°C.

(*a*) Four samples, laboratory prepared. (*b*) Two samples. (*c*) One sample.

[1] Figures in brackets denote limits specified in British Standard Specification 628 for Coconut Oil; refractive index at 40°C., 1·4485–1·4492; free fatty acids (calculated as lauric acid), ≯5%.

[2] Figures in brackets denote limits specified in British Standard Specification 652 for Crude Palm-kernel Oil; refractive index at 40°C., 1·449–1·451; free fatty acids (calculated as lauric acid), ≯6%.

[3] The average Wijs iodine value for over 1,000 samples examined by Ellis and Hall (J.S.C.I. 1919, **38**, 128T) was 18·6 for the crude oils and 18·1 for the refined oils, the minimum and maximum values being 15·6 and 22·9 respectively.

able from it) depends on the care with which the drying process is conducted. In many of the larger estates outside Ceylon hot-air drying is employed, and in a few places, modern systems of kiln- or furnace-drying (rotary driers, vacuum driers) have been installed, which yield a product of very high quality. Strictly sun-dried copra contains, on the average, 50% of fat; kiln-dried copra of good quality should contain about 4–6% of water and yield about 65% of oil with a free fatty acid content of less than 1% (*cf.* E. B. Copeland, "The Coconut," 1931). In certain types of kiln-dried or hot-air dried copra, the percentage of oil may rise to over 70%.

The copra is expressed in oil mills in a manner similar to that in which oil-seeds generally are worked up. In India, quite good results are obtained in native mills of the pestle and mortar type, but in the Philippine Islands, and other up-to-date tropical establishments, the oil for export is expressed in modern machinery of the same type as is current in Europe or in the United States. Owing to the high oil content, copra is expressed in two stages at a temperature of 60–65°, box-presses (Anglo-American type), cage-presses or expellers being employed; the practical yield varies from 63% to 66%, according to the proportion of oil in the copra. The quality of the oil and the proportion of free fatty acids[1] depend upon the quality and condition of the raw material. The press-cake obtained as a by-product of the expression, which contains from 6–10% of oil (when prepared in modern mills), and about 20% of proteins, is used as a cattle-food or fertiliser; the preparation of a press-meal suitable for human consumption has been proposed (*cf.* Parker and Brill, Philippine J. Sci. 1917, A, **12**, 87).

Coconut oil expressed in the tropics, as well as copra, is now largely shipped in bulk: the copra may be unloaded by mechanical means similar to those employed for discharging grain (*cf.* A. W. Allen, Chem. Met. Eng. 1923, **29**, 614); the oil is melted (if necessary) by means of steam-coils situated in the ships' tanks before pumping into shore-tanks.

In temperate climates, coconut oil is a solid white fat of bland taste having a peculiar, but not unpleasant, odour of coconut meat. The odorous substances, which are present in very small amount, consist chiefly of methyl heptyl ketone and methyl nonyl ketone (Haller and Lassieur, Compt. rend. 1910, **151**, 697; Salway, J.C.S. 1917, **111**, 407; Brooke, Philippine J. Sci. 1926, **30**, 201). These two ketones, together with certain other volatile ketones, carbinols, etc., are removed in the deodorizing and refining of coconut oil for edible purposes. When crude coconut oil is stored for long periods in the liquid condition, a waxy sediment may be formed, from which a purified wax (yielding myricyl alcohol and cerotic acid upon saponification) can be recovered, which is stated to be suitable for use as an ingredient of polishes (Tanchico, Philippine J. Sci. 1935, **57**, 423); this sediment is not to be confused with any "foots" or remains of the press-meal, which are normally removed by filtering the crude oil immediately after expression.

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[1] In reporting the free acidity of coconut oil, etc., it is usual to express the percentage of free fatty acids in terms of lauric acid.

The usual ranges of analytical characteristics of coconut oil are shown in Table I on page 240.

It may be noted in passing that *coconut parings oil, i.e.* the dark oil recoverable from the brown skin (testa) of the coconut kernel, which is shaved off in the preparation of desiccated coconut for confectionery, has a higher iodine value (21–60) and lower saponification value (221–241) than the oil from the inner tissues of the kernel; similar differences are also found between the corresponding rind and kernel oils in the case of palm-kernels and babassu kernels (*cf.* Allan and Moore, J.S.C.I. 1925, **44**, 61T, 94T; Wittka, Z. deut. Oel- u. Fett-Ind. 1925, **45**, 417).

The composition of the fatty acids and glycerides of coconut oil is shown in comparison with the figures for other oils of the same group in Table II:

TABLE II.

(*a*) Percentage Composition of the Fatty Acids of Fats of the Coconut Oil Group.
(*b*) Constituent Glycerides of the Fats (probable composition).

Fatty Acids.	Coconut oil.[1]	Palm-kernel oil.[2]	Cohune nut oil.[3]	Babassu fat.[4]	Murumuru fat.[5]	Tucum fat[6]	Gru-gru fat.[6]	Coconut parings oil.[7]
			(*a*) *Percentage.*					
Caproic	*c.* 0·5	—	trace	0·1	—	—	—	—
Caprylic	7·9–9·5	3	7·5	6·5	1·1	1·3	7·8	2(?)
Capric	4·5–7·6	3–7	6·5	2·7	1·6	4·4	5·6	2
Lauric	45–51	47–52	46·5	45·8	42·5	48·9	44·9	28
Myristic	16-18·5	14–15	16·0	19·9	36·9	21·6	13·4	22
Palmitic	7·5–9	7·5–9	9·5	6·9	4·6	6·4	7·6	12
Stearic	2–3	1–2	3·0	—	2·1	1·7	2·6	1(?)
Oleic	5–8	16–18·5	10·0	18·1	10·8	10·8	16·5	23
Linolic	1–2·6	1·0	1·0	—	0·5	0·4	1·6	10
		(*b*) *Glycerides Present in the Oil (Probable Approximate Composition)*						
Fully saturated triglycerides—								
Wt.-%	81–84	63	—	—	—	70	64·5	—
Mol.-%	84–86	66	—	—	—	73	69	—
Mono-unsaturated-di-saturated glycerides (mol.-%)	10·5–12	25	—	—	—	18	22·0	—
Di-unsaturated-mono-saturated glycerides (mol.-%)	3·5	9	—	—	—	9	9	—
Fully unsaturated glycerides (mol.-%)	probably absent (less than 5%)							

[1] Collin and Hilditch, J.S.C.I. 1928, **47**, 261T; Collin, Biochem. J. 1933, **27**, 1366; Armstrong, Allan, and Moore, J.S.C.I. 1925, **44**, 61T; Taylor and Clarke, J. Amer. Chem. Soc. 1927, **49**, 2829.

[2] Collin and Hilditch, *l.c.*; Armstrong, Allan, and Moore, J.S.C.I. 1924, **43**, 207T; 1925, **44**, 143T.

[3] Hilditch and Vidyarthi, J.S.C.I. 1928, **47**, 35T.

[4] Heiduschka and Agsten, J. pr. Chem. 1930, [II] **126**, 53.

[5] Saraiva, Mem. Inst. Chim. Rio de Janeiro, 1929, No. 2, 5; André and Guichard, Compt. rend. 1925, **181**, 228.

[6] Collin, Biochem. J. 1933, **27**, 1366 (sap. vals. 243·6, 252·4; iodine vals. 15·8, 17·1 for tucum and gru-gru fats respectively).

[7] Allan and Moore, J.S.C.I. 1925, **44**, 61T, 94T.

Trilaurin is substantially absent, all the glycerides present being mixed glycerides containing two or three different acid radicles, among which dilauro-myristins appear to predominate (Collin and Hilditch, J.S.C.I. 1928, **47**, 261T). The individual glycerides shown in Table III have been isolated and identified in coconut, palm-kernel, and babassu oils respec-

TABLE III.

Glyceride.	Coconut oil. M.p. °C.	Palm-kernel oil. M.p. °C.	Babassu oil. M.p. °C.
Caprylo-lauro-myristin	15·0	—	—
Caprylo-myristo-olein	—	13·9	—
Dilauro-myristin	33·0	33·4	34·9
Lauro-dimyristin	38·1	40·0	36·1
Dimyristo-palmitin	45·1	45·2	45·7
Myristo-dipalmitin	—	51·4	—
Dipalmito-stearin	55·0	—	55·9

tively, by Bömer and Schneider (Z. Unters. Nahr.-Genussm. 1924, **47**, 61), and by Bömer and Hüttig (Z. Unters. Lebensm. 1938, **75**, 1).

In consequence of the high content of acids of low molecular weight (the mean molecular weight of the total fatty acids of coconut oil, for instance, averages 209 as compared with 270–290 for other fats such as palm oil, olive oil, etc.), the yield of glycerol from the saponification of the nut oils (theoretically 13·5–14·1%) is higher than the yield (theoretically 10·3–11%) from other soap-making fats.

Refined and deodorised coconut oil (or palm-kernel oil, *v. infra*) is used to an enormous extent as a raw material for the manufacture of margarine, and accounts, in fact, for some 60–66% of the total fats consumed for this purpose in the United States. In Europe, the proportion of coconut oil employed for margarine is lower (some 20–30% of the total fats used) owing partly to replacement by palm-kernel oil and, especially, to the rapidly increasing use of hydrogenated whale oil.

It is also used as an ingredient of shortenings and as a cooking fat ("vegetable butter"), especially on the Continent, where such preparations as *beurre végétal* and *palmine* consist almost entirely of palm-kernel or coconut oil; in the tropics, also, coconut oil is commonly employed as a cooking oil.

Coconut stearin (iodine value 4–7, m.p. 27°–32°C., saponification value 250–260), which is obtained by filter-pressing cooled refined coconut oil so as to remove the more liquid glycerides, is used as a chocolate—and confectionery—fat (*q.v.*). Lightly hydrogenated (hardened) coconut oil is also used for the same purpose. The expressed liquid portion—"*coconut olein*"—is used in the United States for frying confectionery nuts or for soap-making. A considerable quantity of technical coconut stearin, prepared by pressing inferior grades of the oil, was formerly used in the manufacture of night-lights (*v.* CANDLES).

The technical grades of coconut oil are used in enormous quantities in the manufacture of soaps. Owing to the low content of unsaturated acids, and the presence of a large proportion of saturated acids of low molecular weight, the sodium soap of coconut oil (or palm-kernel oil, etc.) possesses great hardness and the power to retain considerable quantities of water without becoming soft and also a high solubility and good lathering properties in cold water and in salt water. Further, coconut oil soaps are not thrown out of solution ("salted out") by moderate concentrations of salt, as is the case with the soaps of other fats; hence the nut oils constitute the essential raw material for the manufacture of *marine soaps* for use in sea-water. Owing to the hardness, solubility, and ready lathering power of its soap, coconut oil (or palm-kernel oil) is also an important ingredient of most other types of soap, and, especially, of quick-lathering household soaps, flakes, shampoos, shaving soaps, etc., intended for use in luke-warm water.

The nut oils further differ from other types of soap oils in that they are not easily saponified by dilute caustic alkalis; on the other hand, they are so readily converted into soap by means of concentrated caustic solutions that a simple mixing of the oil with the equivalent quantity of strong lye at about 40°–60°C. suffices to initiate the reaction, which proceeds spontaneously to completion with the evolution of heat. Accordingly, coconut oil is extensively employed for the manufacture of soaps by this so-called "cold process."

Minor amounts of coconut oil are used in the manufacture of pharmaceutical and cosmetic preparations, confectionery fillings, and lubricants.

Owing to its high Reichert-Meissl value, coconut oil, or margarine mixtures containing it, may be used to adulterate butter. Methods for the detection of coconut oil in butter or margarine are based on the detection and estimation of the insoluble volatile fatty acids (caprylic and capric acids) through the analytical determinations of the *Polenske value* (*cf.* Salkowski, Z. anal. Chem. 1887, **26**, 582; Polenske, Arb. Kaiserl. Gesundh.-amt. 1904, 545; Lewkowitsch, "Oils, Fats, and Waxes," 6th ed., vol. 2, pp. 843 *et seq.*); *Bertram A- and B-values* (Bertram, Bos and Verhagen, Chem. Weekblad, 1923, **20**, 610; Z. deut. Oel- u. Fett-Ind. 1924, **44**, 459, ; Bertram, van der Steur, and Verhagen, Chem. Weekblad, 1925, **22**, 549; *cf.* Kuhlmann and Grossfeld, Z. Unters. Nahr.-Genussm. 1925, **50**, 339; (with Baumann), *ibid.* 1926, **51**, 27); *caprylic acid value* (Grossfeld, Z. Unters. Lebensm. 1928, **55**, 354), or *residual number* ("Restzahl"; *cf.* Grossfeld, *ibid.* 1932, **64**, 433). For the detection of the nut oils on the basis of their high content of lauric and myristic acids, *cf.* Shrewsbury and Knapp, Analyst, 1910, **35**, 385; 1912, **37**, 3; Elsdon and Bagshawe, *ibid.* 1917, **42**, 72; Elsdon, *ibid.* 295; Grossfeld and Miermeister, Z. Unters. Lebensm. 1928, **55**, 529; *ibid.* **56**, 423. A qualitative test for the detection of coconut oil in butter fat, which is based upon the microscopical appearance of the crystals obtained on re-crystallising the fat from ether, is described by Hinks (Analyst, 1907, **32**, 160; *see* Lewkowitsch, *l.c.*, pp. 857–858). Similar methods are applied for the detection of coconut oil, etc., in cacao butter (*q.v.*, *cf. also* Cohn, Z. angew. Chem. 1924, **37**, 304; Kulhmann and Grosfeld, *ibid.* 1926, **39**, 24; Härtel and Maranis, Z. Unters. Nahr.-Genussm. 1924, **47**, 205) and soap. Methods for the estimation of *butterfat* in mixtures containing coconut oil (*e.g.* margarine, chocolate) depend upon the determination of the content of *soluble volatile acids* (butyric and caproic acids) in the fat: reference may be made to the methods of Kirschner (Z. Unters. Nahr.-Genussm. 1905, **9**, 65; *cf.* Bolton, Richmond and Revis, Analyst, 1912, **37**, 183; Cocks and Nightingale, *ibid.* 1928, **53**, 322; Soc. Pub. Anal., Anal. Comm. Rept., *ibid.* 1936, **61**, 408; van der Laan, Rec. Trav. chim. 1932, **41**, 724): of Kuhlmann and Grossfeld (Z. Unters. Lebensm. 1925, **50**, 336: calculation from the *Reichert-Meissl* and *saponification values*, *cf.* Pritzker, *ibid.* 1929, **58**, 592): of Kuhlmann and Grossfeld (Z. Unters. Lebensm. 1926, **51**, 31; Grossfeld, *ibid.* 203; *ibid.* 1927, **53**, 381; determination of *butyric acid value*): and of Bertram, Bos and Verhagen (*l.c. supra:* determination of *A*- and *B*- values).

Since coconut oil and palm-kernel oil are so closely similar, differing chiefly in the amount of insoluble volatile acids present (Polenske value), it is extremely difficult, and may be impossible, to decide by analysis which of the two is present in a mixture of other fats (*e.g.* margarine), if no information as to origin is available. The determination of the composition of a mixture of the two nut oils is seldom required, as these fats are rarely adulterated the one with the other; approximate methods for the purpose depending chiefly upon slight differences in the composition of the "Polenske acids" from the two fats are described by van Kregten, Chem. Weekblad, 1915, **12**, 788; Blichfeldt, J.S.C.I. 1919, **38**, 150T; Stokoe, *ibid.* 1921, **40**, 57T; Gilmour, Analyst, 1925, **50**, 119; Elsdon, *ibid.* 1927, **52**, 63.

Palm-kernel Oil is obtained from the seed-kernels of the oil-palm *Elaeis guineensis* Jacq., which is indigenous to West Africa but also cultivated in the Dutch East Indies, Malaya, and other tropical countries. More than 95% of the palm kernels entering world-trade, however, come from Africa—British West Africa, French W. and Equatorial Africa, and the Belgian Congo being the principal producing areas; in the Asiatic regions the palm kernel industry is subordinate to the production of palm oil, and of minor importance at present. The "palm nuts" (*i.e.* the "stones" of the drupaceous fruits) are separated from the oleaginous fruit-pulp when the latter is worked up for the production of palm oil. The "nuts" are dried by exposure to the sun or in kilns sufficiently to loosen the kernels (seeds) within the shells, and the comparatively thin shells are cracked by native hand-labour or by machinery. The kernels are then separated from the shell-fragments by screening or by flotation in brine or clay-water (sp.gr. 1·1–1·5), dried if necessary, and exported in bulk to Europe or the United States. Unlike palm oil and coconut oil, palm kernel oil is not prepared (except for local or native consumption) in the palm-growing regions, the exports being confined to the shelled kernels. In Europe, etc., the kernels are crushed and expressed in the usual way in two stages at 45°–60°C., yielding 43–45% of oil on the large scale. A certain amount of oil is also recovered (in Europe) by extraction with solvents.

The press-cake contains 6–8% of oil and about 2·5% of nitrogen : it is employed in the feeding of dairy cows and other farm animals (*cf.* "Use of Oil Cakes and Extracted Meals," Ministry of Agriculture and Fisheries, Bull. No. 11, 2nd ed., 1937; Anon., Bull. Imp. Inst. 1915, **13**, 151, 446 ; C. Crowther *et al.* J. Agric. Sci. 1917, **8**, 429, 451 ; W. Godden, *ibid.* 419).

Palm-kernel oil is white to pale yellow in colour and resembles coconut oil in composition (*cf.* Tables I, II, III), appearance, and odour; as in the case of coconut oil, the characteristic aroma appears to be due largely to the presence of methyl nonyl ketone (Salway, J.C.S. 1917, **111**, 407). It is used for the same purposes as coconut oil; pressed "*palm nut stearin*" like the corresponding "coconut stearin," is employed as a chocolate fat, and the "*palm nut olein*" for soap-making. Palm kernel oil is generally regarded as slightly inferior to coconut oil and, as a rule, commands a lower price; the choice between the two fats is, however, largely influenced by geographical and politico-economic considerations and trading custom. Thus, before the Great War, Germany held a virtual monopoly of the palm kernel crushing industry, exporting the surplus oil to the United Kingdom and other countries, and since 1925–26 has recaptured her position as premier producer and consumer of the oil, in spite of the growth of important palm kernel crushing industries in the United Kingdom, France and other countries. Imports of palm kernels have been of the order of 250,000–300,000 tons per annum from 1927–1935 (374,000 tons in 1936 and 322,500 tons in 1937) into Germany, and 130,000–160,000 tons per annum into England over the same period (*c.* 200,000–250,000 tons per annum from 1920–1926) ; French imports of the kernels, which were only of the order of 12,000 tons per annum in 1928–1933, have latterly shown a notable increase to 119,400 tons in 1936 (69,000 tons in 1937). Total imports of kernels into the principal importing countries have been 594,200, 735,800, and 675,050 tons in 1935, 1936, and 1937 respectively (*cf.* "Review of Oil and Fat Markets," 1937, H. M. Faure & Co. ; for a detailed survey up to 1932 of the production and trade in palm kernels and palm kernel oil in British and foreign countries, *cf.* "Survey of Vegetable Oil Seeds and Oils, vol. 1, Oil Palm Products," Empire Marketing Board, E.M.B. 54, 1932, H.M.S.O.).

For the determination of palm kernel oil in mixtures, *see under* Coconut Oil.

Babassu Oil is obtained from the kernels of the Brazilian babassu palm, *Orbignya speciosa* Barb. Rodr. (=*Orbignya Martiana*),[1] The woody endocarp ("shell") is extremely hard, and considerable difficulty has been experienced in devising machinery capable of splitting this shell without causing excessive damage to the 2–6 small kernels (which only weigh about 4–6 g. each) contained therein. The kernels contain from 63–70% of fat (*cf.* Tables I, II, III), which closely resembles coconut oil and is used for similar purposes. The woody shells may be used as a fuel, or subjected to destructive distillation for the recovery of acetic acid, etc., and metallurgical charcoal. Babassu fat is one of the principal native fats of Brazil, and since about 1915 considerable quantities of the kernels have been exported to Europe, and, more recently, to the United States. As in the case of the coconut, the press-cake is suitable for use as cattle-food (*cf.* Anon., Bull. Imp. Inst. 1929, **27**, 286; "The Babassu," Ministry of Agric., Rio de Janeiro, 1930; Arié, Arch. Inst. Biolog. São Paulo, 1931, (4), 301; Heiduschka and Agsten, *l.c.*, Table II).

Cohune Nut Oil, from the seeds of *Orbignya cohune* Mart. Dahlgren (=*Attalea cohune*

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[1] When babassu nuts first appeared on the market they were frequently wrongly attributed to the fibre palm ("piassava") *Attalea funifera* Mart.

Mart.) indigenous to British Honduras and Central America, has so far been of little commercial importance, owing largely to lack of development on the agricultural side of the industry, and to the difficulties experienced in providing machinery in place of laborious hand-labour to crack the small hard nuts. The kernels (amounting to 8–10% of the whole fruit) contain from 48–70% of fat (*cf.* Tables I, II), which is, as a rule, slightly softer than coconut oil (*cf.* Bull. Imp. Inst. 1914, **12**, 237; 1934, **32**, 409; Hilditch and Vidyarthi, J.S.C.I. 1928, **47**, 35T).

Murumuru Fat, from the thin-shelled seeds of another Brazilian palm, *Astrocaryum murumuru* Mart., is a hard, brittle fat resembling coconut stearin, and is similarly employed as a chocolate fat.

Although it may be included among the nut oils for convenience, it will be seen from Table II that murumuru fat contains a much smaller proportion of caprylic and capric acids than do the typical fats of the group (the Reichert-Meissl and Polenske values are correspondingly low), and in this respect it approaches the fats of the Dika group, although the content of myristic acid is much lower than in the latter case.

Similarly, the kernel fats of the palms *Astrocaryum tucuma* Mart. (Collin, Biochem. J. 1933, **27**, 1366) and *Areca catechu* (the areca or betel-nut palm) (Rathje, Arch. Pharm. 1908, **246**, 702) have a high content of lauric and myristic acids, but are comparatively poor in the lower acids; these fats have no commercial significance other than for local consumption in the countries of origin.

Khakan Fat, which is chemically very similar to coconut oil, is not derived from a palm but from the unrelated plant *Salvadora oleoides* Done (fam. Salvadoraceæ), and will be discussed under KHAKAN FAT.

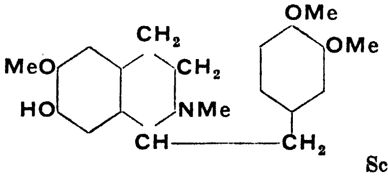
E. L.

COCOSITOL, m.p. 342°, optically inactive, a natural inactive form of inositol, is identical with scyllitol and quercine (Hugo Müller, J.C.S. 1912, **101**, 2383). It was found by him in the leaves of two species of *Cocos*. (*C. plumosa* and *C. nucifera*). The term scyllitol only is retained.

E. F. A.

CODAMINE, $C_{20}H_{25}O_4N$, m.p. 126–127° (hexagonal prisms from Et_2O), is a minor opium alkaloid. The base was first isolated from opium by Hesse (Annalen, 1870, **153**, 66). It reacts strongly alkaline, is moderately soluble in H_2O and very soluble in EtOH. It gives a green colour with ferric chloride, and nitric acid dissolves the alkaloid forming a dark green liquid.

Späth and Epstein (Ber. 1926, **59**, [B], 2791) obtained *d*-laudanosine by methylation of codamine and have conclusively demonstrated that the alkaloid is a laudanosine derivative with a phenolic OH-group in 7-position



Schl.

CODEINE, $C_{18}H_{21}O_3N,H_2O$, an isoquinoline alkaloid, exists in Turkey opium in the proportion of about 0·75% ,while in the Persian or Indian varieties the average is about 2·25%.

CODEONAL. Combination of codeine diethylbarbiturate, 2 parts, and sodium diethylbarbiturate, 15 parts, in tablet form. It is a sedative and hypnotic (*Knoll, Ludwigshafen; Pharmaceutical Products, London*). B.P.C.

COD-LIVER OIL, in the narrowest sense, is the oil obtained from the livers of the European and American cod-fish, *Gadus morrhua* L. (*G. callarias*), and the Japanese cod (" madara " or " tara "), *G. macrocephalus* Tilesius; in ordinary practice, however, which is sanctioned by the definitions of the pharmacopœias of the various countries, the term " cod-liver oil " includes the equivalent liver oils from allied species of *Gadus* or of the family *Gadidæ*, *e.g.* the pollack (*G. pollachius*), the coal-fish or saithe (*G. virens*, *G. carbonarius*, *Pollachius virens*), hake (*Merluccius merluccius*), ling (*Molva molva*), the Japanese *Pollachius Brandtii*, Jordan and Snyder. In Japan, another species of cod, the " suketodara " (" sukeso-dara ")—*Theragra chalcogramma* Pallas (*Gadus chalcogramma*)—is caught in large quantities, but up to the present the liver-oil has not been used for medicinal purposes.

The cod appear annually at certain seasons of the year in enormous shoals in the coastal regions of the northern seas in latitudes above 45°N.; and, correspondingly, important fishing grounds have grown up on the coasts of Norway, Scotland, Iceland, Newfoundland, on both eastern and western coasts of Canada and the United States, and off the shores of Japan and Siberia. As a result of the introduction of factory ships, even more remote fishing-grounds, such as those at Bear Island, Spitsbergen, can be developed for the production of first-class oils. Whilst the oldest and probably the best-known commercial fishing-grounds are those of Norway, whence cod-liver oil (" Bergentran ") was exported (for leather-dressing) as early as the fifteenth century, the Newfoundland industry is also of considerable antiquity, and records exist of the export of "train oil " (cod-oil) to England from the seventeenth century. This area is now becoming increasingly important for the production of high-grade medicinal oils, the bulk of which are exported to Canada and the United States. Both in Newfoundland and Norway, the preparation of medicinal cod-liver oil is conducted under strict Government supervision. The production of medicinal oils on the east coast of the United States and in Japan is also considerable. Until recently the interests of the English native industry were restricted to the technical " cod " oils, but of late years efforts have been made to promote manufacture of domestic medicinal oils.

In the Newfoundland and Lofoten fisheries of Norway the catch consists exclusively of cod, but in the Finmark fishery of Norway and the English coastal fishery, saithe, pollack, hake, ling, and other closely allied members of the cod family are included. The liver oils of these fish, however, are closely similar in chemical composition to that of the true cod, and since they are equal to, or in some cases superior to, pure cod-liver oil in vitamin potency, no objection to their presence is made. In the Lofoten fishery the fish are taken during the spawning season in a fasting condition, and the livers are poorer in oil than those obtained from the fish which are caught in the Finmark or " Lodde "-fishing season, and off Newfoundland, when the cod is feeding actively and in a well-nourished state.

In the oldest process for the recovery of cod-liver oil, the livers, after removal from the fish, were heaped up in barrels and allowed to undergo spontaneous putrefaction in order to decompose the liver cells and permit the oil to exude, which was drawn off at intervals as the rotting proceeded, in fractions ranging from pale brown to almost black in colour; the process might be accelerated by exposing the barrels to the sun. Some improvement in the quality of the oil was effected by careful selection of sound livers, and the removal of blood of the gall-bladders and other visceral matter before treatment, but, nevertheless, even the best oils prepared by the " rotting " method were contaminated with decomposition products of the liver tissue (organic bases) and possessed a rank, fishy odour and nauseous taste.[1] This crude method of preparing the oil is now practically obsolete and, except in a few primitive installations producing low-grade oils, has been replaced by the " steaming process." In the original process introduced by Charles Fox in Newfoundland (1848, *cf.* Munn, Montreal Pharm. J. 1914, **25**, 192) and developed by P. Möller in Norway, 1853 (*cf.* Möller, " Cod-liver Oil and Chemistry," 1895), the fresh, sound, washed livers were rendered in steam-jacketed pans, but to-day it is more usual to " cook " the livers with open steam (at a pressure of from 30–100 lb./sq. in.) which is blown directly into the mass of fresh livers contained in an open or covered pan.

For the production of the finest (medicinal) grade of oil, tin-lined pans or vessels of non-corroding metal, are employed, and only sound livers in the freshest possible condition are taken ; all diseased or discoloured livers are rejected and worked up separately for the technical grades of oil. The gall-bladders are removed, and the livers are thoroughly washed before steaming, which is continued for a sufficient time (about 30 minutes) to ensure the destruction of any fat-splitting enzymes, which might otherwise cause deterioration of the oil during subsequent storage. The oil which separates freely from the livers is dipped off, strained, and allowed to stand in order that traces of liver tissue and moisture may settle out, and the purification is completed, if necessary, by filtration, centrifuging, or treatment with fuller's earth; finally, the oil is packed into tin-lined barrels for transport or storage. In order to prevent deterioration of the oil and loss of vitamin-potency through oxidation, exposure of the oil to air and light is minimised throughout the operations. (For further details of the preparation of medicinal cod-liver oil in Norway, Newfoundland and Iceland, *cf.* Zilva and Drummond, J.S.C.I. 1922, **41**, 280T; 1923, **42**, 185T, 250T; Drummond and Hilditch, " Relative Values of Cod-liver Oils from Various Sources," Empire Marketing Board, Pub. No. 35, 1930; Le Gall, Rev. Trav. Off. Pêches marit 1930, **3**, 1030 ; Chabre, Thesis, Paris, 1936 ; Macpherson, Bull. 3, Fish Sect. Dept. Nat. Resources, Newfoundland, 1937).

The medicinal oil obtained in this manner is consumed as " congealing oil " in those countries where the pharmacopœia or popular taste raises no objections to such an oil, which deposits a solid " stearin " when exposed to low temperatures. In England and certain other countries, however, the pharmaceutical trade prefers, and the pharmacopœia prescribes, a " non-freezing " oil, which does not set at low temperatures ; this is prepared by " refining " or chilling the crude oil at temperatures between 0°C. and −10°C. in order to precipitate the higher-melting glycerides (" stearin ") which are filtered off at about 0°C., leaving a yield of about 75–80% of a clear " non-freezing " oil. The separated " stearin " (consisting actually of mixed glycerides of saturated and unsaturated acids) may be pressed in order to recover any entrained liquid oil (which is added to the second grade of oil) and is sold as the best quality " fish stearin " for soap manufacture.

The steamed liver-pulp remaining in the rendering-pan may be boiled up again with steam before it is finally pressed, yielding in both cases oils of good quality which are employed as a vitamin-active supplement in the feeding of poultry and cattle. The final residue of liver-tissue is dried and converted into liver-meal for animal feeding. In general commerce, the expression " cod-liver oil " is restricted to the medicinal oils intended for human or animal nutrition, whilst the term " cod-oil " (" brown cod-oil," " brown oil ") is used for the technical oils which are obtained by steam-rendering (or, more rarely, by the rotting process) from livers which, on the score of condition or freshness, are unfit for the production of medicinal oil; where other fish besides cod are included in the catch, the oil is known commercially as " coast cod oil." The cod-oils, in general, have a high acid value and rank odour, and are contaminated with impurities derived from the decayed liver-cells; the use of such oils for the feeding of animals is to be deprecated, especially as there is some evidence that oils from putrid livers may be definitely toxic. The crude " unracked " cod-oils contain considerable quantities of stearin which are removed by chilling and filtering or settling, and used in soap-making or as " fish-tallow " in leather currying. Cod-oils find extensive use in the leather industries, where the raw oil is employed in the chamoising process and in the currying (stuffing) and oiling of heavy leathers ; further, considerable quantities of sulphonated (sulphated) cod-oil, *e.g.* *Turkey-red oils*, which is prepared by treating the oil with concentrated sulphuric acid are employed for the oiling-off of heavy leathers and for the fat-liquoring of light leathers and chrome-tanned leathers. Technical cod oils are also employed in the manufacture of lubricating greases and low-grade soaps. The dried, pressed liver meal recovered as a by-product of cod-oil manufacture is utilised as "fish manure."

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[1] Details of the " rotting " process and the early steaming process are described by Möller, " Cod-liver Oil and Chemistry," London, 1895 ; *cf. also* Lewkowitsch, " Oils, Fats, and Waxes," 6th ed., vol. II, p. 437.

Pure medicinal cod-liver oils of pharmacopœia quality are pale in colour and have only a slightly fishy odour and taste; in consequence, probably, of the different feeding conditions, the oils from Newfoundland and Iceland possess a distinctly deeper yellow colour than the Norwegian oils. (N.B. This inherent colour is quite distinct from the discoloration of oils which have been prepared from stale livers or by bad methods.)

The analytical characters of medicinal cod-liver oils are illustrated in Table I, except where otherwise stated, the figures refer to oils produced on the large scale from batches of mixed livers from fish of both sexes, different size, etc. Naturally, oils extracted in the laboratory from individual livers of fish of different size, etc., show wider extremes of variation.

TABLE I.

CHARACTERISTICS OF COD-LIVER OILS.

	Medicinal oils (mostly non-congealing).[1]	Pharmacopœial requirements (non-congealing oils).[2]	Crude whole (*i.e.* congealing) medicinal oils.[3]	Pure cod-liver oils.[4]	Japanese cod-liver (madara) oils.[5]
Sp.gr. . . .	0·920–0·9288/ 25°C.	0·922–0·929/ 15·5°C. (B.P.) 0·918–0·927/ 25°C. (U.S.P.)	—	0·924–0·929/ 15·5°C.	0·9243-0·9397/ 15°C. (0·924–0·9298)
Ref. index . .	1·474–1·4798/ 20°C.	1·4705–1·4745/ 40°C. (B.P.)	—	1·4705–1·4728/40°C.	1·4742–1·4803/ 20°C. (1·4765–1·4868)
Saponification value . . .	175–197 (usually 180–190)	180–190 (B.P.) 180–192(U.S.P.)	175–188 (*a*) 181–189 (*b*,*c*) 172–198·5(*d*)	181–189	174·5–190·7 (183–189)
Iodine value .	147–183 (usually 150–170)	155–173 (B.P.) 145–180 (U.S.P.)[6]	153–162 (*a*) 142–185 (*b*) 159–174 (*c*) 140–185 (*d*)[6]	154–172	143–205 (152–182)
Acid value .	0·5–3·5	≯1·2 (B.P.) ≯2·8 (U.S.P.)	0·6–2·4	—	0·4–5·0 (0·5–12)
Unsaponifiable matter . .	0·9–1·7%	1·5% (B.P.) 1·3% (U.S.P.)	—	0·96–1·52%	0·6–4·5% (0·6–1·0)

The non-freezing oils have, as would be expected, somewhat higher iodine values and refractive indices than the crude oils from which they have been derived (*cf.* Holmes and Pigott, *l.c.*; Kawai, *l.c.*, 1933), but the differences lie within the range of variation shown by the crude oils. There is no significant difference in vitamin contents between corresponding specimens of crude and non-congealing oils.

The acid value of the best oils is frequently less than 0·5; the second quality of oil for animal consumption is only slightly inferior to the pharmacopœial oils, but usually possesses a stronger fishy taste and slightly darker colour, the acid value may be as much as 2 (*cf.* proposed specification for veterinary cod-liver oil, Drummond and Hilditch, *l.c.*; for review of the literature on the use of cod-liver oil in animal feeding, *see* J. R. Manning, U.S. Bur. Fisheries, Doc. No. 1065, 1929, p. 333). The technical cod oils have lower iodine values, depending upon the amount of oxidation the oil has suffered, and high free acidities. The following figures

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[1] *Cf.* Lewkowitsch, "Oils, Fats, and Waxes," vol. II; A. D. Holmes, Ind. Eng. Chem. 1924, **16**, 1181; Holmes and Clough, Oil and Fat Ind. 1927, **4**, 403; Ender and Jermstad, Pharm. Zentralh. 1930, **71**, 193.

[2] Brit. Pharm., 1936 Addendum to B.P. 1932; United States Pharm. XI, 1936. In pharmacy, cod-liver oil is known as *Oleum Morrhuae* or "*Oleum jecoris aselli.*"

[3] Drummond and Hilditch, Empire Marketing Board 35 (1930), pp. 43–48; oils from (*a*) Norway, (*b*) Scotland, (*c*) Newfoundland and Iceland; (*d*) oils from east coast of N. America, Holmes and Pigott, Ind. Eng. Chem. 1926, **18**, 188; Oil and Soap, 1936, **13**, 225.

[4] N. Evers and Smith, Quart. J. Pharm. 1932, **5**, 337.

[5] K. Kawai, J. Pharm. Soc. Japan, 1933, **53**, No. 10, 183; the figures shown are range values for a number of oils prepared from selected groups of fish; the figures in brackets show the ranges for specimens of oil produced commercially. *Cf.* Hirose, J. Soc. Chem. Ind. Japan, 1930, **33**, 172B. The oil content of individual livers of "madara" ranged from 10–65%. "Suketo-dara" liver oil shows a slightly lower sp.gr. (0·9216–0·9294) and lower iodine value (136–161) than "madara" liver oil (Kawai, *l.c.*).

[6] For *Oleum Morrhuae non-destearinatum* (*i.e.* the entire oil), the "United States Pharmacopœia," XI allows the iodine value to be between 125 and 180.

(due to Holmes, Clough and Owen, Oil and Fat Ind. 1929, **6**, (No. 10), 15) for twenty oils of various grades, including sun-rotted oils, are illustrative: sp.gr. 0·9193–0·9266 at 25°, n_D^{20} 1·480–1·483, saponification value 184–194·5, iodine value 146·3–168·6, unsaponifiable matter 1·2–2·8%, free fatty acids 7–20·2%. Somewhat higher percentages of unsaponifiable matter may be found in coast cod oils.

The approximate quantitative composition of the fatty acids of cod-liver oil is indicated in Table II, in which the corresponding figures for some allied and closely similar fish-liver oils are included for comparison:

TABLE II.

PERCENTAGE COMPOSITION OF FATTY ACIDS OF FISH LIVER OILS

(Guha, Hilditch and Lovern, Biochem. J. 1930, **24**, 266; *cf.* Drummond and Hilditch, *l.c.*)

Fatty acids.	Liver oils.				
No. of carbon atoms per mol.	Cod.		Saithe.	Hake.	Ling.
	(a)[1] %	*(b)*[2] %	%	%	%
Saturated Acids.					
C_{14}	3·5–6	2	6·5	4·5–7	5
C_{16}	6·5–10	14	12–13	11–13	13
C_{18}.	0–0·5	1	0–0·5	0·5	1
Unsaturated Acids.					
C_{14} (—2H)	0–0·5	2	trace	trace	trace
C_{16} (—2H)	16–20	10	9·5–14·5	8–17	13
C_{18} (—3H)	25–31	26	29·5–31	18–34	32·5
C_{20} (—xH)	26–31·5 (x=5–6)	25 (x=5·5)	24·5–26·5 (x=5)	25–31 (x=4–5)	24 (x=6)
C_{22} (—xH)	10–14 (x=7)	20 (x=7·4)	10–16·5 (x=7)	14–16 (x=6)	11·5 (x=7)
C_{24} (—xH)	?	<1 (x=?)	?	?	?

Figures in brackets denote average unsaturation of each fraction, *e.g.* (—2H) denotes one double bond; (—3H), a mixture of perhaps mono- and di-ethenoid acids, averaging one and a half double bonds.

[1] Range of analyses of Scotch, Norwegian, and Newfoundland cod-liver oils.

[2] North Sea cod-liver oil: average unsaturation of the C_{18} unsaturated acids = —3·3 H. Harper and Hilditch, J.S.C.I. 1937, **56**, 322T.

The saturated fatty acids (10–15% of the total acids) consist chiefly of myristic and palmitic acids, with traces of stearic acid (Guha, Hilditch and Lovern, *l.c.*; Toyama, J. Soc. Chem. Ind. Japan, 1926, **29**, 172B). The unsaturated acids include a large proportion of the mono-ethylenic *zoomaric* ($\Delta^{9:10}C_{16}H_{30}O_2$), *oleic* ($\Delta^{9:10}C_{18}H_{34}O_2$), *gadoleic* ($\Delta^{9:10(?)}C_{20}H_{38}O_2$), and *cetoleic* ($\Delta^{11:12}C_{22}H_{42}O_2$) acids (H. Bull, Ber. 1906, **39**, 3570; Toyama, J. Soc. Chem. Ind. Japan, 1926, **29**, 624; 1927, **30**, 154B, 155B; 1934, **37**, 14B); myristoleic ($C_{14}H_{26}O_2$), and selacholeic ($\Delta^{15:16}C_{24}H_{46}O_2$) acids are present in minor amount (Toyama and Tsuchiya, *ibid.* 1935, **38**, 684B). More highly unsaturated acids of the C_{20} and C_{22} series, including docosahexaenoic acid ($C_{22}H_{32}O_2$) (*cf.* Farmer and Van den Heuvel, J.C.S. 1938, 427), are also important constituents; ***stearidonic acid*** ($C_{18}H_{28}O_2$) and *arachidonic acid* ($C_{20}H_{32}O_2$) have been identified by Suzuki (Proc. Imp. Acad. Tokyo, 1929, **5**, 165) and ***nisinic acid*** ($C_{24}H_{36}O_2$) by Toyama and Tsuchiya (J. Soc. Chem. Ind. Japan, 1934, **37**, 531B). The "*jecoleic acid*" and "***therapic acid***" of the early investigators (*cf.* Heyerdahl, in F. P. Möller's "Cod Liver Oil and Chemistry," 1895) were probably more or less impure preparations of gadoleic and stearidonic acids respectively.

The older reports concerning the occurrence of lower saturated (volatile) fatty acids, such as acetic, butyric, and capric acids, as well as of organic bases in cod-liver oil were caused by the presence of decomposition products of the oil and liver tissue in the old "rotted" oils.

The unsaponifiable matter of cod-liver and cod-oils amounts normally to 0·7–2·8%,[1] although a much larger proportion has been reported in individual cases of the oils from single lean livers of old, large fish (*cf.* K. Kawai, J. Pharm. Soc. Japan, 1933, **53**, No. 10, 183); as a rule, about half the unsaponifiable matter; consists of cholesterol, the remainder comprising the fat-soluble vitamins (*see below*), colouring matters, and other non-sterol constituents including squalene and batyl alcohol (Drummond, Channon, and Coward, Biochem. J. 1925, **19**, 1047), one or two other unsaturated hydrocarbons, and, perhaps, other mono- and di-hydric (aliphatic) alcohols (Wiedemann, *ibid.* 1932, **26**, 264; Kawakami, Bull. Inst. Phys.-Chem. Res. Tokyo, 1933, **12**, 825, 834, 845 (Abstr. 7, 8, 9, publ. with Sci. Papers I. P.-C. R. Tokyo, 1933, **22**, No. 457–467).

Cod-liver oil, even of unexceptionable quality, contains a small amount of iodine, of the order of 3–15 pts./million (*cf.* Hopfer de l'Orme, Hufeland's J. 1836 (April), p. 115; Heyerdahl, *l.c.*; Holmes and Remington, Amer. J. Dis. Children, 1935, **49**, 94). The presence of traces of arsenic (from 1·4 to 5·1 pts./million) in unrefined cod-liver oil from fresh livers has been reported by Holmes and Remington (Ind. Eng. Chem. 1934, **26**, 573) and Luzanski (Tids. Kjemi, 1936, **16**, 56).

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[1] It is possible that some of the extreme differences reported in the literature may be attributable to the different methods employed to extract and determine the unsaponifiable matter (*cf.* S.P.A. Sub. Comm. Rept., Analyst, 1933, **58**, 203).

In common with other fish-liver oils, cod-liver oil gives a red-violet coloration when concentrated sulphuric acid is added to a solution of the oil in chloroform or carbon disulphide; the depth of the colour varies with different oils, and appears to be due to a condensation reaction of some minor constituent of the oil (lipochrome?) associated with vitamin-*A* and analogous to the antimony trichloride colour reaction of the latter (*v. infra*) (*cf.* Drummond and Watson, Analyst, 1922, **47**, 341). With Japanese acid clay, a blue-green coloration is developed (*cf.* Kobayashi, Mem. Fac. Sci. Eng. Tokyo, 1927, **4**, 23). These colour reactions may fail, however, with hydrogenated (hardened) liver oils.

A green colour reaction is observed when a solution of cod-liver (or other fish-liver) oil in glacial acetic acid is treated with a mixture of bromine and chloroform and iodine bromide (Hanus iodine solution) (Tortelli-Jaffe reaction: Tortelli and Jaffe, Chem.-Ztg. 1915, **39**, 14; *cf.* Better and Szimkin, Fettchem. Umschau, 1934, **41**, 225).

Although cod-liver oil seems to have been held in esteem as a domestic remedy for many centuries among the inhabitants of the northern coasts, its systematic use in the treatment of bone-disorders, tuberculosis, and conditions of malnutrition appears to date from the successful clinical trials made at Manchester in the second half of the eighteenth century by Dr. Kay and his colleagues (*cf.* T. Percival, Medical Essays, 1789, II, 354), and despite the nauseous character of the oils available at that time, the popularity of cod-liver oil as a remedy steadily increased through the nineteenth century. The extensive modern use of cod-liver oil in the prophylaxis and cure of rickets and other conditions associated with defective calcium metabolism is now so well known as to be a commonplace. The remarkable therapeutic properties of the oil, which have been variously ascribed to the presence of organic bases, to the presence of traces of iodine, and to the specific nature of the highly unsaturated acids which compose the bulk of the glycerides of the oil, are now attributed primarily to the presence, in comparatively high concentration, of the fat-soluble vitamins-*A* and -*D* (*cf.* Osborne and Mendel, J. Biol. Chem. 1914, **17**, 401; Drummond, Biochem. J. 1919, **13**, 81). (It may be noted, however, that cod-liver oil has recently attracted renewed attention as a source of combined iodine in the treatment of certain deficiency conditions, *cf.* Chidester and others, Nature, 1932, **130**, 544; Science, 1932, **76**, 436.)

The vitamin-*A* activity of cod-liver oil results from the occurrence in the oil of the actual vitamin-*A* itself (as distinct from a precursor thereof, such as carotene), which is present to the extent of some 100–500 pts./million, chiefly in esterified form (Bacharach and Smith, Quart. J. Pharm. 1928, **1**, 539; Reti, Compt. rend. Soc. biol. 1935, **120**, 577; Hickman, Nature, 1936, **138**, 881; Ind. Eng. Chem. 1937, **29**, 1107; Hamano, Sci. Papers Inst. Phys.-Chem. Res. Tokyo, 1937, **32**, 44). Its presence is indicated by a maximum at $\lambda=328$ mμ in the absorption spectrum of the oil or of the unsaponifiable fraction therefrom (K. Takahashi, *et al.* J. Chem. Soc. Japan, 1922, **43**, 826; 1923, **44**, 590; Sci. Papers Inst. Phys.-Chem. Res. Tokyo, 1925, **3**, 81; Heilbron *et al.* Biochem. J. 1928, **22**, 987; 1931, **25**, 20; J.S.C.I. 1931, **50**, 183T), the intensity of which affords an approximately quantitative measure of the vitamin-content of the oil (*cf.* Coward, Dyer and Morton, Biochem. J. 1932, **26**, 1593; Carr and Jewell, Nature, 1933, **132**, 92; Gillam, Heilbron, Morton, Bishop and Drummond, Biochem. J. 1933, **27**, 878; Booth, Kon, Dann and Moore, *ibid.* 1189; Baumann and Steenbock, J. Biol. Chem. 1933, **101**, 547; Chevallier and Chabre, Biochem. J. 1933, **27**, 298; Jones and Christiansen, J. Amer. Pharm. Assoc. 1935, **24**, 1072). This test (the examination being conducted on a solution of the unsaponifiable matter) was recommended as a method of vitamin-*A* assay by the Second International Conference on Vitamin Standardisation (1934), and has been admitted as a subsidiary test in the 1936 Addendum (Appendix IV) to the "British Pharmacopœia" of 1932, where it is regarded as giving a trustworthy indication of the vitamin-*A* content of cod-liver oils which conform in all other respects to the requirements of the "British Pharmacopœia." (As there may be other substances, however, which show a similar absorption in the region of $\lambda=328$mμ, the test may be inapplicable to certain vitamin preparations, etc., and the "British Pharmacopœia" Addendum prescribes that, in the event of any discrepancy between the results of the vitamin-*A* assay by the spectrophotometric method and by the biological method, the value as determined by the latter method should be accepted.)

The presence of vitamin-*A* is also revealed by the blue colour (absorption maxima at $\lambda=$ 572–584 and 617 mμ), which is obtained on treating a solution of the oil in chloroform with antimony trichloride (Carr-Price reagent, Biochem. J. 1926, **20**, 497; *cf.* Analyst, 1931, **56**, 457; 1932, **57**, 302; "British Pharmacopœia," 1932). The intensity of the coloration (which may be measured spectrophotometrically, or by means of a colorimeter under standard conditions) runs roughly parallel to the vitamin-activity of the oil as measured by biological methods, but several instances of discrepancy have been noted, which may be due to the presence of inhibitors in the oil, or perhaps to the presence of an allied but biologically inactive chromogen (*cf.* O. Rygh, Bull. Soc. Chim. biol. 1934, **16**, 609; Ender, Biochem. J. 1932, **26**, 1118; Lovern and others, *ibid.* 1931, **25**, 1341). Better correlation is obtained if the colour test is performed on a solution of the unsaponifiable fraction from the oil (*cf.* Smith and

Hazley, Biochem. J. 1930, **24**, 1942; Church and Norris, J. Biol. Chem. 1930, **87**, 139; Coward and others, Biochem. J. 1931, **25**, 1102; Analyst, 1932, **57**, 368; Emmerie, Nature, 1933, **131**, 364; 1935, **136**, 183). (It may be noted, however, that this colour test, which figured in the 1932 edition of the "British Pharmacopœia" has been discarded in the 1936 Addendum in favour of the spectrophotometric test.) For further details concerning these tests, and of the biological assay of vitamin-*A*, *see* "British Pharmacopœia" Addendum, 1936. An interesting modification of the Carr-Price test, in which a less fugitive violet colour ($\lambda_{max.}=545$ and 475 mμ) is obtained by the use of guaiacol as reagent, is described by E. Rosenthal and Erdélyi (Biochem. Z. 1933, **267**, 119; 1934, **271**, 414; Biochem. J. 1935, **29**, 2112; Rosenthal and Weltner, *ibid.* 1935, **29**, 1036).

The vitamin-*A* activity of cod-liver oil varies within wide limits according to the age and sexual condition of the fish, its place of origin, and its food; cases of oils containing from 210 to 3,400 International Units (I.U.) per gram are reported by Chevallier (Ann. Chim. Analyt. 1936, (iii), **18**, 93; *cf.* Chabre, Thesis, Paris, 1936; *cf.* K. Kawai, J. Pharm. Soc. Japan, 1932, **52**, No. 10, 95; No. 12, 169); the "British Pharmacopœia" Addendum (1936) and the "United States Pharmacopœia," XI (1936), impose a minimal requirement of 600 I.U. per g. of oil. The figures of Chevallier and Chabre, like those of Drummond and Hilditch (E.M.B., No. 35, *l.c.*) support the view that, on the whole, the oils from Newfoundland and Iceland are richer in vitamin-*A* than the Norwegian oils. On the other hand, the Norwegian (Lofoten) oils appear to be richer in vitamin-*D* (*cf.* Poulsson, Nord. Med. Tidsk. 1933, **6**, 886; Amer. J. Pharm. 1934, **106**, 102). The vitamin-D content of cod-liver oil also varies considerably, and is quite independent of the amount of vitamin-*A* present (*cf.* Coward, Dyer and Morgan, Analyst, 1932, **57**, 368; van Esveld, Nederl. Tijds. Geneesk. 1935, **79**, 2924; Kawai, J. Pharm. Soc. Japan, 1934, **54**, No. 5, 87). On the whole, the less the oil content of the cod liver; the greater is the concentration of vitamin-*D* in other words, the depletion of the fat reserves in the liver during spawning, fasting, or ageing of the cod-fish is not accompanied by a corresponding drain on the store of vitamin-D (*cf.* Poulsson, *l.c.*; Kawai, *l.c.*, 1934).

According to K. Kawai (*l.c.*) the same tendency is observable in the case of vitamin-*A* and the blue (Carr-Price) chromogen, very high potencies, and especially high blue-values, being observed in the case of oils from livers which, owing to the age or condition of the cod, were very poor in oil.

Before the anti-rachitic principle (vitamin-*D*) of cod-liver oil had been isolated it became clear from biological comparison of the relative therapeutic efficiencies in tests with different animals (rats and chicks) that the active agent in cod-liver oil was not identical with calciferol (vitamin-D_2), obtained by the irradiation of ergosterol (*cf.* Massengale and Nussmeier, J. Biol. Chem. 1930, **87**, 415, 423; Steenbock and others, *ibid.* 1932, **97**, 249; Russell, Taylor, and Wilcox, *ibid.* 1934, **107**, 735; J. Nutrition, 1935, **9**, 569; Bills, J. Biol. Chem. 1935, **108**, 323); and it has recently been shown by Zucker, Simons, Colman and Demarest (Naturwiss. 1938, **26**, 11) that the vitamin-*D* of cod-liver oil, like the vitamin-*D* which has been isolated (*via* the dinitrobenzoate) from tunny-liver and halibut-liver oils (Brockmann, Z. physiol. Chem. 1936, **241**, 104; 1937, **245**, 96; *cf.* Simons and Zucker, J. Amer. Chem. Soc. 1936, **58**, 2655), is in all probability identical with "*vitamin-*D_3" prepared artificially by the irradiation of 7-dehydrocholesterol (Windaus, Schenk, and Werder, Z. physiol. Chem. 1936, **241**, 100; Grab., *ibid.* 1936, **243**, 63; Folberth, Z. Kinderheilk. 1937, **59**, 329). Vitamin-D_3 has been obtained in the crystalline state (Schenck, Naturwiss. 1937, **25**, 159) and it has been shown that, despite the difference in the chemical constitution (the side-chain of the molecule), vitamin-D_3 has the same antirachitic potency (40 million I.U. per g.) as calciferol when tested on rats (International method). Like the rat, the human subject appears to be equally sensitive to both forms of vitamin-*D*, that is to say, the administration of an equal number of units (as measured by the usual tests with rats) of calciferol, vitamin-D_3, or cod-liver (or other active fish-liver) oil produces quantitatively the same therapeutic effect (*cf* Eliot, Nelson, Barnes, Browne and Jenss, J. Pediatrics, 1936, **9**, 355, 761). The chick, on the other hand, discriminates between the different vitamins, for, whilst it readily utilizes vitamin-D_3 or the cod-liver oil vitamin, it is most inefficient in its use of calciferol, so that some fifty times as many (rat-)units (I.U.) of calciferol are needed to evoke the same response as any given number of units of cod-liver oil or vitamin-D_3. The possibility that more than one form of vitamin-*D* may occur in fish-liver oils is mooted by Bills, *et al.* J. Amer. Med. Assoc. 1937, **108**, 13; J. Nutrition, 1937, **13**, 435).

The vitamin-*D* of cod-liver oil appears to be present partly in the free state and partly as esters (Hickman, Nature, 1936, **138**, 881; Ind. Eng. Chem. 1937, **29**, 1107). The amount in the oil is probably of the order of 2–8 parts per million, but up to the present only biological methods of comparing the potencies of different oils have been adopted (*cf.* suggested method in "British Pharmacopœia" Addendum, 1936, Appendix XV, also article VITAMIN-D); both the "British Pharmacopœia" Addendum and the "United States Pharmacopœia" (1936) require a minimum potency of 85 I.U. per g. of oil. A photometric method for the assay of vitamin-*D*, which has been proposed by L. Fuchs and Beck (Pharm. Presse, Wiss.-Prakt. Heft, 1933, **38**, 81, 93) requires further investigation.

The origin of the vitamins in cod-liver oil—whether they are merely ingested as such with the food of the fish and stored in the liver, or what part, if any, is played by the fish in the synthesis of either vitamin—is still obscure, and reference may be made to the following memoirs for further discussion of this issue; Drummond, Biochem. J. 1922, **16**, 518; Bills, J. Biol. Chem. 1927, **72**, 751; Wimpenny, Sci. Rep. Fisheries

Invest. Ser. 2, vol. II, No. 5, 1929, London; Drummond, Nature, 1930, **126**, 398; Gunther, Collin, Drummond and Hilditch J. Expt. Biol. 1934, **11**, No. 2, 173; Copping, Biochem. J. 1934, **28**, 1516.

The statements of Taylor and Nelson (Taylor, Iowa State Coll. J. Sci. 1931, **5**, No. 4, 355; Nelson, Ind. Eng. Chem. 1927, **19**, 840) that cod-liver oil also displays vitamin-*E* activity is contrary to the observations of Sure (J. Biol. Chem. 1927, **74**, 37, etc.) and require confirmation, especially since cod-liver oil figures as a regular constituent of satisfactory vitamin-*E*-free diets for experimental work (Bacharach, private comm.).

According to Waterman and van Dijk (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 1206), cod-liver oil may be hydrogenated at low temperatures under controlled conditions without impairing the vitamin activity.

Whilst cod-liver oil itself is still largely used in medicine, its place has to some extent been taken by other fish-liver oils,[1] such as halibut-liver oils which have a much greater vitamin content and require a correspondingly smaller dosage, or by more palatable concentrates of the vitamins extracted from the oil. Various processes for the extraction of the unsaponifiable matter from cod-liver oil for this purpose have been patented; further, high-vacuum short-path distillation (" molecular distillation ") of the oil has been proposed for the separation of the active principles (*cf.* Waterman, van Dijk, and Imperial Chemical Industries, B.P. 452442; Hickman and Eastman Kodak Co., U.S.P. 1925559).

Concerning the alleged toxic effects of the administration of cod-liver oil, *cf.* Agduhr, Z. Vitaminforsch. 1934, **3**, 99; Upsala Läkareforen Förh. 1933-4, **39**, 307; 1934-5, **40**, 183; Norris and Church, J. Biol. Chem. 1930, **89**, 437; W. M. Cox, Jr., and Roos, Bull. Johns Hopkins Hosp. 1934, **44**, No. 6, 430; Bell, Gregory and Drummond, Z. Vitaminforsch. 1933, **2**, 161; Thatcher, Lancet, 1936, **230**, 20; L. L. Madsen, *et al.* Cornell Univ. Agric. Exp. Stat. Mem. 1935, No. 178; Burack and Zimmerman, J. Nutrition, 1937, **14**, 535.

Concerning the use of cod-liver oil as a healing dressing for burns and other wounds, *see* W. Löhr, Zentr. Chirurgie, 1934, **61**, 1686; *cf.* Lancet, 1934, **227**, 367; Steel, *ibid.* 1935, **229**, 290; Stevenson, *ibid.* 1376.

Modern methods in the preparation of cod-liver oil emulsions are described by Rothenkirchen (Pharm.-Ztg. 1934, **79**, 804). (Concerning the stability of vitamin-*A* in cod-liver oil emulsions, *see* Griffiths, Hilditch and Rae, Analyst, 1933, **58**, 65).

Preparations of the soaps of the fatty acids ("British Pharmaceutical Codex"), or of the unsaturated acids only, of cod-liver oil are used in medicine (as a sclerosing agent in, for example, the treatment of varicose veins) under the name of *sodium morrhuate* (*cf.* Haines, Lancet, 1933, **224**, 748); the acids themselves are occasionally referred to as "morrhuic acid."

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E.L.

CŒLESTINE. A mineral, $SrSO_4$, a source of strontium.

CŒLINBLAU, CŒRULEUM *v.* BLUE CERULEAN; *v.* COBALT.

CŒRULEÏN, *Anthracene green* (*v.* ALIZARIN AND ALLIED DYESTUFFS.

CO-ENZYMES, CO-ZYMASE. Following Buchner's famous discovery of an agent in the filtered liquid contents of yeast cells, capable of fermenting sugar solutions in the absence of living cells, Harden and Young (Proc. Chem. Soc. 1905, **21**, 189) discovered that this agent could be separated by ultra-filtration into a thermostable dialysable part—the co-zymase—and a thermolabile non-dialysable part—now called apozymase. The addition of the boiled dialysate to the inactive apozymase restored its activity. This was in part due to the presence of inorganic phosphates and in part to an organic substance. In fact, Buchner's zymase is a mixture of many enzymes and the process of alcoholic fermentation is a complicated series of reactions which have only recently been elucidated by Embden and by Meyerhof.

In brief, the sugar is phosphorylated before being decomposed, the primary product of decomposition being the phosphoric ester of a triose, probably glyceraldehyde, which by dismutation gives rise to a mixture of phosphoglyceric acid and phosphoglycerine.

In the next stage the glyceric acid passes by loss of water under the influence of an enzyme into phosphopyruvic acid. At this stage the co-enzyme comes into action combining with the phosphoric acid group and forming free pyruvic acid. The labile co-enzyme-phosphate then reacts with glucose to form hexosephosphate and regenerated co-enzyme. The pyruvic acid is decomposed by carboxylase to acetaldehyde and carbon dioxide, the former being subsequently reduced to ethyl alcohol. The co-zymase has been identified as a complex diphosphodinucleotide containing nicotinic acid (pyridinecarboxyamide) and adenine.

In the voluntary and heart muscles, a somewhat similar series of changes takes place, the essential difference being that the pyruvic acid is reduced to lactic acid. The co-enzyme is adenylic acid, the system being

adenyl pyrophosphate
$\longleftrightarrow$ adenosine diphosphate
$\longleftrightarrow$ adenosine-5-phosphate

(Meyerhof and Kiessling, Biochem. Z. 1935, **283**, 83; Lohmann and Schuster, *ibid.* 1935, **282**, 104).

Adenylic acid was found to be a riboside-5-phosphoric acid of adenine by Embden and

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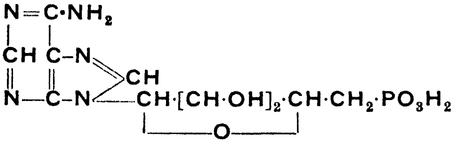
[1] Vitamin-active liver oils are also obtained from the burbot (*Lota* sp.), a fresh-water fish allied to the cod (*cf.* Nelson, Tolle and Jamieson, U.S. Bur. Fisheries, Investigational Rept. No. 12, 1932; Poulsson, Norsk. Mag. Laegevidenskap. 1931, **92**, 125), and the tunny (*Thunnus thynnus* L.), the latter oil being especially rich in vitamin-*D* (*cf.* Brockmann, *l.c.*; Schmidt-Nielsen, Kgl. Norske Videnskab. Selsk. Forh. 1930, **3**, 407).

Schmidt (Z. physiol. Chem. 1929, **181**, 130); Levene and Jacobs (Ber. 1911, **44**, 746); and Levene and Stiller (J. Biol. Chem. 1934, **104**, 299). Gulland and Holiday (J.C.S. 1936, 765) established its formula as adenine-9-riboside-5-phosphoric acid,



Thus the co-enzymes of alcoholic fermentation, of lactic acid dehydrogenase, of muscle and of Warburg's (Biochem. Z. 1935, **282**, 1, 157) oxidation system are all closely related or identical (Adler, Euler, and Hellström, Nature, Dec. 5th, 1936, p. 968).

Co-zymase is widely present in yeasts, in muscle, in various animal organs and tissues, particularly the liver, and in certain bacteria. It is rare in the higher plants and absent from certain races of bacteria, in which another form of sugar degradation must take place (Myrbäck and Euler, Ber. 1925, **57**, 1073; Virtanen and Simola, Z. physiol. Chem. 1927, **163**, 284).

It is obtained as a colourless, easily soluble powder (a recent summary relating to co-zymase is given by Myrbäck, Ergebnisse der Enzymforschung, 1933, **2**, 139–168).

There is evidence afforded by purification by means of copper (Euler, Albers and Schlenk, Z. physiol. Chem. 1935, **234**, 1) or by heating (Euler and Vestin, Z. physiol. Chem. 1935, **237**, 1) that co-zymase is a molecule possessing groups whose powers of activating enzymic reactions are independent of each other. Andersson (Z. physiol. Chem. 1935, **235**, 217) concludes that the substance has two independent reaction centres, one in an adenylic acid grouping concerned with phosphorylation and the other with oxidation-reduction.

E. F. A.

COFFEE. The beverage known as "coffee" is prepared by infusion of the beans or seeds of *Coffea arabica*, an evergreen shrub indigenous to North East Africa and Arabia. The use of coffee orginated in Abyssinia, whence it was introduced into the neighbouring Mohammedan countries, its physiological action in promoting sleeplessness being regarded as of advantage to those attending the prolonged religious ceremonies. In spite of objections by the priests on the ground that it was an intoxicating beverage, its popularity became firmly established there and has continued. The use of coffee was extended through Europe during the first half of the seventeenth century and in 1652 it was introduced into England. Here it rapidly attained popular favour and during the following two centuries "coffee houses" played an important part in the social life of English cities. In 1847 the importation of coffee reached a maximum of nearly 17,000 tons, but since then it has declined, owing, no doubt, to the greatly increased use of tea and also, in some measure, to the introduction of coffee substitutes. For the past decade the clearances for home consumption have been as follows :

Year (ended 31st March).	Clearances, tons.
1926–1927	15,981
1927–1928	15,897
1928–1929	15,453
1929–1930	15,306
1930–1931	16,709
1931–1932	16,340
1932–1933	15,521
1933–1934	14,782
1934–1935	14,763
1935–1936	15,052

These quantities may be compared with the importations into the United States, which are over 700,000 tons per annum.

The importations into the United Kingdom are almost equally from Empire and non-Empire sources, although since 1933 the balance has been slightly in favour of the former, which in 1935–1936 reached nearly 53% of the total. This trend in favour of the Empire products (which are chiefly from British East Africa and India) is probably due to increased imperial preference under the Ottawa agreement.

The coffee tree belongs to the natural order Cinchonaceæ which embraces, according to Lindley and Paxton, two species, *C. arabica* and *C. paniculata*, but some botanists distinguish many other species. Four commercial types distinct from each other are now grown: (1) Arabian or Mocha coffee, having short, upright branches with a brittle leaf, and seeds usually single in the berries. (2) Jamaica coffee, bearing longer and more pliable branches, a tougher leaf, and seeds almost always double in the berries. (3) East India or Bengal coffee, of which the leaf is smaller than that of the Jamaica variety and the berry very small. (4) Liberian coffee is taller and has larger leaves and fruit than the other varieties, but, owing to its coarse flavour, it was not until recently of much commercial use. It has, however, now attained importance, on account of its hardy habit and power of resistance to disease, and is largely cultivated by grafting on to its stem the more delicate and highly esteemed Arabian coffee. Trees growing wild in the Cingalese jungle attain a height of 14–18 ft., but, under cultivation and subjection to systematic pruning, the plant rarely exceeds 9 ft. and is usually less.

Production.—Within the tropics the coffee tree thrives best at 1,200–3,000 ft. above sea level, but grows at a height of 6,000 ft. When the mean temperature is about 70° it may grow as far north as latitude 36°. It is cultivated in the West Indies, Mexico, Central America, Brazil and Cayenne ; in Western Africa, Egypt, Mozambique and Natal ; in Arabia, India, Ceylon, Siam, Sumatra, Java, Celebes and other parts of the Eastern Archipelago, Fiji and the islands of the Pacific. According to data extracted from the "International Year Book of Agricultural Statistics" the total world production of coffee for the years 1930–1935 was as follows.

Year.	Production (thousands of tons).
1930–1931	2,365
1931–1932	2,035
1932–1933	2,330
1933–1934	2,472
1934–1935	2,078

Of these totals Brazil produced, on the average, about 67%. Brazil is also the greatest exporter of coffee, a preponderance clearly demonstrated by the following data published by the Brazilian Government:

	(Thousands of tons.)			
	1933	1934	1935	1936
Exports from Brazil—				
To Europe	353	344	368	337
To United States	486	490	489	470
To southern ports	68	64	75	80
Exports from other countries—				
To Europe	263	294	271	323
To United States	220	205	244	278

Although the exportation from Brazil has shown little variation, the production is restricted by the fact that the trees, after a year of heavy crops, require a season to recuperate. For commercial reasons much of the coffee produced in Brazil has been withheld from the market and to the end of 1935 over 2 million tons had been destroyed. According to data published by the Empire Marketing Board in 1932 the area under cultivation in the British Empire was about 368,000 acres compared with about 10,000,000 acres in foreign countries, whilst of the total world exportation 3% was from Empire countries.

Cultivation.—The method of forming plantations varies somewhat in different countries. The surface soil should be good and the subsoil not very heavy. Probably the best soil is that known in Brazil as "terra roxa," a top soil of red clay 3 or 4 ft. thick with a subsoil of gravel. Virgin forest land is as a rule found to be very suitable. The soil should not be very wet and steep slopes are unsuitable owing to rain wash. The loss due to this cause may be repaired by good manure—well rotted dung and ground bones being the best. According to Beckley (Kenya Colony Dept. Agric. Bull. 1932, 16) ground rock phosphate and bone meal form the most effective fertiliser. Shelter from wind is most important. The young plants may be reared from seeds in nurseries, whence they are transplanted to their permanent position, or they may be gathered out of the old plantations. The age at which this is done varies. Thus in Brazil transplanting usually takes place when the plants are 2 years old, whilst in the West Indies the plants are about 6 months old. Fruit is produced in the fourth year and continues to be gathered for several years. The tree blossoms and bears fruit practically all the year round and the fruit takes about four months to ripen. There is thus in some cases an almost perpetual crop, but, as a rule, there are two principal harvest seasons in the year. Leaf and berry fall, caused by disease, has been the subject of considerable investigation, particularly in Kenya (Dept. Agric. Bull. 1932, 17, 20 ; 1934, 3). The conclusions indicate that there is no relation between the incidence of the disease and the chemical composition of the soil, and the addition of lime and fertilisers does not protect trees predisposed to attack. Whilst it is stated that Bordeaux mixture is not in itself a satisfactory remedy, certain modifications of the mixture are suggested which will prevent germination of the fungus spores. According to Sladden (Bull. Agric. Congo Belge, 1932, **23**, 329) infection of the harvested bean with *Stephanderes hampei* can be corrected by fumigation with turpentine, which does not injure the germinative power of the beans. Layers of the beans are alternated with layers of cotton cloth soaked with 1 ml. of turpentine per 100 sq. cm. and allowed to stand in hermetically sealed containers for 3 days at 26°C.

The coffee fruit consists of a bilobed berry somewhat resembling a small elongated cherry, by which term it is described commercially. As the fruit ripens the fleshy pericarp changes colour from green through yellow and red to a deep crimson. When dried, it blackens and becomes hard and brittle, resembling a shell or husk. Beneath the skin of the pericarp is a saccharine and somewhat glutinous pulp containing the seeds, which are usually double, lying face to face, but sometimes occurring singly. Each seed or bean is enclosed in two membranous coverings—an outer, consisting of tough buff-coloured tissue, technically known as "parchment," which becomes loose and readily separates on drying ; and an inner film of thin white tissue, closely adherent to the bean, and known as the silver skin.

Harvesting.—The principal methods in vogue for gathering and preparing the coffee berries for commerce are as follows. In Arabia, Egypt, and the Antilles the berry is left on the tree till completely dried, when it is easily shaken down and the dry outer envelope and the "parchment" removed by pounding in a mortar, beating with a flail, or simply rubbing in the hands. In other countries the berries are gathered by hand as soon as ripe but not dry and are spread out on the ground in layers from 4 to 6 in. deep. These are exposed to the sun's heat for 3 or 4 weeks with frequent turnings with a spade, when the bean becomes easily removable from the fruit by gentle trituration. This process, however, sometimes imparts to the coffee a disagreeable flavour due to putrefactive changes in the pulp, and recourse is therefore frequently had to artificial heat. The most modern method is to "pulp" the berries by crushing between rollers so as not to injure the beans, which are then subjected to a fermenting process in tanks, with or without the addition of water, after which they are separated from the pulp by "washing" and dried, either by the sun or by artificial means. Coffee beans in the form of "cherry" rarely enter into commerce but frequently retain the parchment and inner skin, which, however, are removed by rolling and winnowing before the beans are roasted. The beans are then graded into different sizes by special machinery which also separates the round, or "pea-berries," from the ordinary flat-faced beans. The following table will indicate the variations in size :

	No. of seeds in approx. 50 ml.
Fine brown Java	187
Fine Mysore	198
Fine Neilgherry	203
Costa Rica	203
Good ordinary gautemala . .	207
Good La Guayra	210
Good average Santos . . .	213
Fine long berry Mocha . . .	217
Good ordinary Java . . .	223
Fine Ceylon plantation . . .	225
Good average Rio	236
Medium plantation (Ceylon) .	238
Manila	248
Ordinary Mocha	270
West African	313

Roasting.—The object of roasting coffee is to develop its aroma and to destroy its toughness so that it may easily be reduced to powder. The process is conducted in cylinders heated by coke fires or gas. The cylinders are usually made of strong wire gauze to permit the escape of steam and other volatile products immediately they are formed. Great care is necessary to ensure an equable roasting of all the beans and to attain the exact point at which the process should cease. If, on the one hand, the process is not carried far enough, the flavour of the bean is not developed and the coffee is hard to grind. On the other hand, overheating causes carbonisation and the production of a strong empyreumatic flavour, which renders the coffee infusion nauseous. The loss in weight is from 15 to 18%, of which approximately one half is due to moisture and the rest chiefly to volatile products derived from the fat and from the sugar during caramelisation. A certain small amount of caffeine is also lost. At the same time an oily substance caffeol (*q.v.*) is developed, which, although present only in very small proportion, imparts to roasted coffee much of its characteristic aroma. The most favourable temperature for developing the maximum aroma during roasting is a little above 200°C. After roasting it is most important that the beans should be cooled rapidly. This is effected by spreading them on a large sieve through the meshes of which they cannot pass, but through which air is forcibly drawn by means of a powerful exhaust connected with a closed chamber immediately below the sieve.

During the process of roasting various substances are driven off. Bernheimer (Wien Akad. 1880, **81**, (2), 1032) found that, after water vapour, there is a sudden evolution of carbon dioxide probably due to a process of destructive distillation accompanied by dehydration and polymerisation. Trigg (R.K.D. Bull. No. 3). In the interior of the bean reducing conditions obtain whilst oxidation takes place on the exterior. Bernheimer (Monatsh. 1880, **1**, 456) found that 50 kg. of raw coffee beans roasted in a revolving drum yielded about 5 litres of liquid distillate with approximately 680 g. of solid floating thereon. The filtered liquid was yellow in colour and had the fragrant odour of coffee. It was found to contain caffeine, caffeol, acetic acid, quinol, methylamine, and acetone. The solid portion was found to consist chiefly of palmitic acid. In contradiction to the above workers Hagen (Trop. Agric. 1922, **59**, 269), whilst admitting that marked changes take place during normal roasting, considers that the constituents of the bean are not dissipated, there being a transformation into substances which contribute to the aroma of the roasted product. Erdmann (Ber. 1902, **35**, 1846) attributed the aroma of roasted coffee to traces of acetic acid, furfural, valeric acid, an unstable nitrogenous compound, and a phenolic body resembling creosote, whilst other workers have suggested that the main odoriferous principle is some unidentified nitrogen compound.

Deterioration after Roasting.—Since the essential oil rapidly escapes after the bean is broken up coffee should not be ground until required for infusion. Apart from this physical consideration, however, the bean undoubtedly gradually undergoes a process of deterioration due to chemical changes and known in the trade as " staling." Trigg (*l.c.*) suggests that this is due to hydrolysis and oxidation, causing alteration and volatilisation of the aromatic principles. Tunnett and Eddy (Food Ind. 1930, **2**, 401) suggest that the taste of stale coffee is probably due to the oxidation of the oil. They found that staleness developed only slightly faster in ground than in unground coffee. Their work has been further developed by Bengis (Food Ind. 1935, **7**, 490), who states that roasted coffee contains about 15–16% of oil and fat, much of which is unsaturated. The oil extracted from freshly roasted coffee carries in it the aroma and flavour bearing substances which are easily oxidised. On the other hand, the oil extracted from stale coffee has a rancid, disagreeable flavour. It absorbs much less oxygen which, it is therefore suggested, plays an important part in the " staling."

Chemical Composition.—Many investigators have published data relative to the chemical composition of coffee. Levasic (Arch. Pharm. 1876, [iii], **8**, 294) found the following percentage values :

	Gummy matter.	Caffeine.	Fat.	Tannic and Caffetannic acids.	Cellulose.	Ash.	Potash.	Phosphoric acid.
Finest Jamaica plantation	25·3	1·43	14·76	22·7	33·8	3·8	1·87	0·33
Finest green Mocha . .	22·6	0·64	21·79	23·1	29·9	4·1	2·13	0·42
Ceylon plantation . . .	23·8	1·53	14·87	20·9	36·0	4·0	—	0·27
Washed Rio	27·4	1·14	15·95	20·9	32·5	4·5	—	0·51
Costa Rica	20·6	1·18	21·12	21·1	33·0	4·9	—	0·46
Malabar	25·8	0·88	18·80	20·7	31·9	4·3	—	0·60
East Indian	24·4	1·01	17·00	19·5	36·4	—	—	—

Commaille (Mon. Sci. 1876, [3], **6**, 779) found in undressed Mysore coffee :

	%
Fat	12·68
Glucose	2·60
Legumin-casein . . .	1·52
Albumen	1·04
Caffeine	0·42–1·31
Ash	3·88

Five different commercial types of Ceylon coffee gave the following results published by the Imperial Institute :

	Percentage.		
	Min.	Max.	Average.
Moisture . . .	10·1	10·6	10·3
Caffeine . . .	2·1	2·4	2·3
Crude proteins .	11·2	13·4	12·5
Fat	6·1	7·8	6·9
Carbohydrates .	49·3	52·1	50·7
Crude fibre . .	13·5	15·3	14·4
Ash	3·3	3·5	3·4

It will be observed that these samples were unusually rich in caffeine whilst the proportion of fat was low. Data published by the same authority for coffee grown in Sierra Leone were more normal, approximating closely to the values for Arabian coffee, *viz.* moisture 8·2, caffeine 1·3, crude proteins 8·5, fat 10·1, nitrogen-free extract 50·6, crude fibre 17·8, and ash 3·5%. Valenzuela (Philippine J. Sci. 1929, **40**, 349) gave the average percentage composition of seven varieties grown in the Philippines as follows : moisture 9·86, caffeine 1·87, fat 8·71, reducing sugar 5·22, crude fibre 19·65, nitrogenous substances 12·95, and ash 4·10.

Caffeine.—Of the substances which have been isolated from coffee that which has attracted most attention is caffeine. It is interesting that the two other popular beverages, tea and cocoa, contain respectively the alkaloids theine, identical with caffeine, and theobromine, which is closely related to it. It has been suggested that the caffeine is present as caffetannate, whilst Gorter (Annalen, 1908, **358**, 327) states that the caffeine occurs in coffee combined with potassium as potassium-caffeine-chlorogenate,

$$C_{16}H_{17}O_9K(C_8H_{10}N_4O_2)_2.$$

Caffeine also occurs in many other commodities and the method of its determination has therefore received considerable attention. The percentage of caffeine in coffee, and particularly in the so-called de-caffeinised coffee, is so low, however, that some methods suitable for general application are of little value in this connection and only those especially devised for coffee need be mentioned. Lendrich and Nottbohm (Z. Unters. Nahr.-Genussm. 1909, **17**, 241) propose the extraction with carbon tetrachloride, and transference to solid paraffin which is then extracted with water. After clearing with potassium permanganate the aqueous solution is evaporated to dryness, the residue extracted with chloroform, dried, and weighed. Fendler and Stüber (Z. Unters. Nahr.-Genussm. 1914, **28**, 9) whilst confirming this method suggest certain modifications which render the estimation more expeditious. Vautier (Mitt. Lebensm. Hyg. 1919, **10**, 272) suggests that at least 10 g. of the sample should be taken and first extracted with ether. The crude caffeine should then be extracted with chloroform, evaporated to dryness with sodium carbonate, again extracted with chloroform five or six times, the extracted caffeine then being dried and weighed. Bonifazi (Mitt. Lebensm. Hyg. 1926, **17**, 307) confirms Vautier's method. Various modifications have been suggested. Thus Ugarte (Chemia, 1930, **7**, 490) proposed that before extraction the material should first be carbonised cautiously in a Kjeldahl flask, care being taken that none of the white vapour formed is allowed to escape. Bonn and Desgrez (Ann. Falsif. 1931, **24**, 546) propose that after extraction the residue from evaporation should be taken up in 10 ml. of 5% HCl and an excess of silicotungstic acid solution added. After heating and prolonged standing the precipitate is filtered off, ignited and weighed, the weight of the precipitate multiplied by 0·2236 representing the hydrated caffeine. Helberg (Mitt. Lebensm. Hyg. 1933, **24**, 54) states that best results are obtained if the powdered coffee is first rubbed with a mixture of lime and quartz sand. Herndlhofer (Mikrochem. 1932, **12**, 227) proposed an interesting nephelometric method for measuring the turbidity produced by adding sodium phosphotungstate to a caffeine solution. The amount of caffeine in "decaffeinised" coffee varies considerably according to the nature of the original coffee and the process employed. Guillaume and Lefranc (Bull. Sci. Pharmacol. 1935, **42**, 14) state that the quantity of soluble substance in "caffeine-free" coffee is only two-thirds of that in the untreated material and the caffeine may be as low as 0·0004%. Braunsdorf (Z. Unters. Lebensm. 1933, **65**, 460) found that in an infusion of 8–11 g. in 150 ml. "caffeine-poor" coffee gave up to 22 mg. of caffeine, "caffeine-free" coffee gave up to 8·8 mg., and coffee gave up to 72 mg. Bonifazi (Mitt. Lebensm. Hyg. 1926, **17**, 307) found that 20 g. of decaffeinised coffee usually contains about 8·4 mg. of caffeine. For the estimation Borgmann (Apoth.-Ztg. 1931, **71**, 56) proposes a method involving Soxhlet extraction, whilst Clifford (J. Assoc. Off. Agric. Chem. 1931, **14**, 553) supports a method based upon sublimation.

Caffetannic acid, which is said to be present in coffee, is uncertain in its composition and very susceptible to change. According to Gorter (Annalen, 1908, **358**, 327) it is associated with chlorogenic acid, which is present in the proportion of 6·3–7·7% in the raw bean and 3·2–4·5% in the roasted coffee (Hoepfner, Z. Unters. Lebensm. 1933, **68**, 238). The same worker (Chem.-Ztg. 1932, **56**, 991) states that in the presence of acetic acid, chlorogenic acid gives a brilliant carmine coloration on the addition of $NaOH$. His method has been modified by Plücker and Keilholz (Z. Unters. Lebensm. 1934, **68**, 97). Jurany (Z. anal. Chem. 1933, **94**, 225) proposes a method involving extraction with alcohol and transfer through solid paraffin to an aqueous solution which is cleared with lead acetate, the optical rotation then giving a measure of the chlorogenic acid present. According to Jurany samples of raw coffee were found by this method to contain 8–9% of chlorogenic acid, *q.v.*

Sugar.—Herfeldt and Stutzer (Z. angew. Chem. 1895, **8**, 469) state that sugar occurs in the raw bean only as a glucoside. This is in contradiction to the findings of other investigators. Thus König and Bell found from 5 to 9% in raw coffee. In support of this finding Bell points out that when the saccharine extract of the beans is boiled with a little dilute sulphuric acid a quantity of glucose is obtained nearly equivalent to the weight of dry extract operated upon, a result inconsistent with the presence of sugar as a glucoside. Bell considers that this sugar is not present as sucrose, but the chemists of the United States Department of Agriculture (Bulletin 13) have isolated cane sugar in considerable amount as pure, well-defined crystals. It is usually accompanied by some invert sugar probably formed during the process of extraction. It is generally admitted that there is practically no sugar in roasted coffee, that present in the raw bean being nearly all caramelised during roasting.

Cellulose.—In coffee this is very hard and very difficult to define under the microscope, especially after roasting, although the chief characteristics of the cellular tissue are more or less retained. It is dissolved by an ammoniacal solution of copper oxide and gives a blue colour with sulphuric acid and iodine. Remnants of the "silver skin" are always present even after roasting, and its structure, a thin membrane with adherent thick-walled, spindle-shaped and hollow cells, is quite peculiar to coffee and a useful means of identification.

Fat v. Coffee Bean Oil.

Protein, chiefly in the form of insoluble albuminoids, occurs in coffee, both raw and roasted, to the extent of from 10 to 14%, the soluble albuminoids constituting about 2%.

Mineral Matter.—The total amount of ash varies from 3·5 to 4·0% in raw, and from 4·0 to 5·0% in roasted coffee. The following percentage compositions are given by the United States Department of Agriculture (Div. of Chem., Bull. 13, 904).

	Mocha.	Mara-calbo.	Java.	Rio.
Sand	1·44	0·72	0·74	1·34
Silica (SiO_2) . .	0·88	0·88	0·91	0·69
Ferric oxide (Fe_2O_3)	0·89	0·89	1·16	1·77
Lime (CaO) . .	7·18	5·06	4·84	4·94
Magnesia (MgO) .	10·68	11·30	11·35	10·60
Potash (K_2O) . .	59·84	61·82	62·08	63·60
Soda (Na_2O) . .	0·48	0·44	—	0·17
Phosphoric acid (P_2O_5) . . .	12·93	13·20	14·09	11·53
Sulphuric acid (SO_3) . . .	4·43	5·10	4·10	4·88
Chlorine . . .	1·25	0·59	0·73	0·48

Ludwig (Arch. Pharm. 1872, [iii], **1**, 482) states that the silica increases from the root upwards to the leaves and pericarp of the fruit, after which it declines in the parchment skin and is nearly absent in the bean.

Physiological.—The primary value of coffee as an article of human consumption is its stimulative property. Indeed, it can, when taken in a strong infusion, have such an exhilarating effect that, as already stated, attempts were made to prevent its use in Mohammedan countries on the ground that it was an intoxicant.

According to Lehmann and Weil (Arch. hyg. 1923, **92**, 58) the action of coffee on the nervous system is to be attributed to the caffeine present. For the same reason coffee is a stimulant to gastric secretion (Haneborg, Acta. Med. Scand. 1924, **61**, 228; and Farrell, North Western Univ. Amer. J. Physiol. 1928, **85**, 672) although Bandoin (Bull. Soc. hyg. aliment, 1920, **11**, 655) found that coffee has a decided retarding effect on peptic and pancreatic digestions which is proportionate to the tannin content. A strong infusion of coffee has a distinct diuretic effect which, probably owing to the action of lecithin, can be inhibited by the addition of milk or (more effectively) cream, Hitzenberger and Roller (Wien. Arch. inn. Med. 1935, **27**, 133). Pietro di Mattei (Arch. Farm. sperim. 1923, **35**, 5) found by experiments on pigeons that roasted coffee had a marked curative effect in cases of polyneuritis, although raw coffee and pure caffeine were without effect.

Adulteration.—Although the adulteration of coffee in this country is now practically non-existent, it is very common abroad and the number and variety of the adulterants are almost unlimited. Many of these are best detected by means of the microscope. Digestion with water affords a ready means of differentiating between the pale soft-walled tissues of the cereals and roots, often used as adulterants, and the dark-coloured and hard-walled tissue of coffee. The cereals may readily be identified by their characteristic starch granules. The chemical differences between coffee and its adulterants are also strongly marked, as the sophisticated products usually show high aqueous extract and sugar and low fat and caffeine contents. The density is also a useful factor in the preliminary examination, that of raw coffee varying between 1·041 and 1·368 and that of roasted coffee between 0·500 and 0·635. In the Paris Municipal Laboratory, Regnault's volumenometer, as modified by Dupré, is used for this purpose. Colouring matters are frequently employed to disguise damaged beans and give them the appearance of superior quality. Among the substances so used are chrome yellow, yellow ochre, indigo, Prussian-blue, azo-dyes, and soapstone for the raw bean; and burnt umber, oxide of iron, and Venetian red for the roasted bean. The inorganic colouring matters are best sought in the ash or in the sediment obtained by shaking the beans in cold water; indigo and Prussian blue by their usual reactions and other colouring matters by extraction with alcohol. Glazing is a process resorted to for the alleged purpose of preserving the roasted beans. The substances used, a mixture of egg albumen with glucose or gum, are said to have the effect of clarifying the infusion. The improved appearance of the beans and increased weight due to the retention of moisture, are probably also important considerations. The latter result is sometimes attained by the addition of sugar before roasting or by steaming the beans and coating them with glycerine, palm oil or vaseline to prevent evaporation of moisture. Bertarelli (Z. Nahr. Genussm. 1900, **3**, 681) describes the adulteration of roasted coffee beans with a solution of borax, which not only gives the beans a glossy appearance but also adds as much as 12% to their weight. Shellac is occasionally used for glazing, and Nottbohm and Koch (Z. Nahr. Genussm. 1911, **21**, 288) draw attention to the fact that shellac is sometimes coloured by arsenic trisulphide. Coffee beans which had been glazed with arsenical shellac were found to be strongly contaminated with arsenic. Zurbriggen and Scheurer (Mitt. Lebensm. Hyg. 1931, **22**, 377) found that many substances used as coatings for coffee can be identified by washing the grains with a suitable solvent, evaporating and comparing the fluorescence of the extract under a mercury lamp with that of pure specimens of the substances suspected.

Although the addition of chicory (*q.v.*) to coffee is often regarded as a form of adulteration, public preference for this admixture justifies the view that chicory is an adjunct to, rather than an adulterant of, coffee if its presence is disclosed at the time of sale. It would appear, however, that chicory is declining in favour, the consumption in the United Kingdom having steadily fallen from 3,200 tons in 1927 to 700 tons in 1936. Chicory has little in common with coffee except a considerable proportion of sugar which is converted into caramel in the process of roasting and thus imparts to the infusion a deep colour, a bitter taste, and an aroma somewhat resembling that of coffee. Smith and Bartell (Univ. of Mich. Dept. of Eng. Research, Sept. 1924) show that, owing apparently to a process of chemical reaction between the caffeol of the coffee and the soluble constituents of the chicory, the aromatic caffeol is held in the infusion. An elaborate research into the nature of coffee and chicory with a view to the detection of adulteration was made at the instance of the Commissioners of Inland Revenue in 1852 by some of the leading botanists and chemists of the day, and the results are of great practical value even at the present time. The following table, prepared during this investigation, shows the sp.gr. at 60°F. of solutions made by treating 1 part of each of the substances named (roasted and finely ground) with 10 parts of water (by weight), raising the mixture to boiling-point for half a minute, then filtering and cooling.

Spent tan	1002·1
Date stones	1002·9
Lupin seed	1005·7
Acorns	1007·3
Peas	1007·3
Mocha coffee	1008·0
Beans	1008·4
Neilgherry coffee	1008·4
Plantation Ceylon coffee	1008·7
Java coffee	1008·7
Jamaica coffee	1008·7
Native Ceylon coffee	1009·0
Costa Rica coffee	1009·5
Parsnips	1014·3
Carrots	1017·1
Black malt	1021·2
Turnips	1021·4
Rye malt	1021·6
English chicory	1021·7
Dandelion root	1021·9
Red beet	1022·1
Foreign chicory	1022·6
Guernsey chicory	1023·2
Mangold wurzel	1023·5
Roasted figs	1024·9
Maize	1025·3
Bread raspings	1026·3

It will be seen from the above table that the low specific gravity of the coffee infusion distinguishes it from roots and cereals, and when chicory is the only substance admixed with the coffee its percentage may be calculated with approximate accuracy by a comparison of the gravity of the infusion of the mixture with the average gravities of coffee and chicory given in the table. As an alternative method Savini (Annali Chim. Appl. 1923, **13**, 217) suggests boiling 10 g. of the sample for 5 minutes with 200 ml. of water. The infusion is then cooled, made up to 250 ml., and filtered ; 25 ml. of the filtrate are evaporated to dryness and the residue weighed. Variation from the normal figure for coffee indicates some form of adulteration. Bunce and Moitra (Analyst, 1932, **57**, 708) state that the average extract obtained from Indian coffee is 28%, which is about 4% higher than is ordinarily assumed for coffee, and that therefore the origin of the coffee must be taken into account in applying the above methods. The relative colouring powers of roasted coffee and chicory afford a further simple test for the presence of chicory or other substances containing caramel. A few grains of the sample are placed on the surface of cold water in a glass vessel, without stirring, when the particles of foreign substance each emit a brownish-coloured cloud, which is rapidly diffused in streaks through the water. Pure coffee affords no appreciable coloration under similar conditions. The chicory readily sinks, whilst nearly the whole of the coffee remains at the surface. If examined under the microscope the sediment of chicory which reaches the bottom of the vessel will be found to exhibit the characteristic large cells with dotted vessels and branching lactiferous ducts. Even to the touch of a needle there is a difference, for whilst chicory under these conditions will feel soft, the coffee grains remain hard. Winter-Blyth ("Foods ; Their Composition and Analysis," p. 368) thus summarises the influence of chicory on the coffee mixture : the respective proportions of gum, fatty matter, tannic and caffetannic acids, and caffeine are decreased, the proportion of sugar is increased, and the constitution of the ash is profoundly modified, especially in the proportion of silica, which is not found to any great extent in coffee ash. In amplification of the last point the following may be accepted as representing the principal differences in the composition of the respective ashes :

	Coffee.	Chicory.
Silica and sand	—	10·69–35·85
Carbonic acid	14·92	1·78–3·19
Sesquioxide of iron	0·44–0·98	3·13–5·32
Chlorine	0·26–1·11	3·28–4·93

There is a marked difference in the proportion of ash soluble in water, that from coffee being about 75–85% and from chicory 21–35%.

"*Decaffeineised*" *Coffee.*—The public demand for "decaffeineised" coffee has resulted in considerable search for a method which, while removing some or all of the caffeine, will yield a product possessing unimpaired the flavour and aroma of the original bean. Many of the processes thus devised have been patented and it is possible that, at least in some cases, commercial considerations have, in part, formed the basis for the favourable claims advanced on their behalf. In any case the so-called "decaffeineised" coffee almost invariably contains some caffeine which may vary from a trace up to 1%. The basic principle underlying nearly all the processes is some form of extraction but the solvents used and the treatment of the beans show wide variation. When an aqueous extraction is relied upon the water may be untreated, rendered alkaline, or loaded by the solution of sugar or other substances, in order to effect the selective removal of the caffeine from the beans. The organic solvents used include benzene, toluene, ketones, alcohols and chloroform. In some cases solvents are used in rotation whilst in others an emulsion of chloroform or benzene with water is used. The extraction sometimes takes place under pressure whilst in other methods the beans are crushed, rolled, or steam-heated before or during the extraction. It is a common practice to remove the last traces of the solvent by passing a current of hot air or steam over the beans at the end of the process. In some cases no attempt is made to conduct a selective extraction. Conditions are imposed which result in substances other than caffeine being removed. The solution is subsequently treated with a solvent in which the caffeine is readily soluble and the residual extract returned to the beans by spraying before roasting. As an alternative to extraction by treatment of the beans with a solvent it is claimed that infusions of coffee can be "decaffeineised" by passing through charcoal or a layer of silica gel.

Substitutes or Imitations, although not very common in the United Kingdom, are more prevalent in the coffee-drinking countries of Europe and America. They are prepared from a variety of different substances. In addition to chicory, these include acorns, beet refuse, bran, cereals (barley, maize, malt, oats, rye and wheat) caramel, carrots, dandelion root, figs, lupin seeds, mangolds, parsnips, peas, beans, coffee husks, cassia seeds, date stones, etc. In general these may be identified by the methods proposed above. These preparations are sometimes offered quite openly as substitutes, but imitation beans have been prepared by mixing any of the above with gum, molasses or other adhesive material and skilfully moulding the mixture into the form of coffee berries. The following are some of the imitations or substitutes which have been placed on the market:

Negro or Mogdad coffee made from the seeds of *Cassia occidentalis.*

Massaendar coffee from the seeds of *Gærtnera vaginata.*

Kunst Kaffee from roasted roots or cereals.

Pelotas coffee and *Coffee surrogate* from ground acorns.

Date coffee from date stones or dried dates mixed with a small proportion of coffee.

"French Coffee" is a description sometimes applied to a mixture of coffee with burnt sugar and a large proportion of chicory. As these ingredients readily absorb moisture on exposure to the air this mixture is usually preserved in tins.

F. G. H. T.

COFFEE BEAN OIL and **WAX.** Apart from a waxy coating on the outer surface of the bean, coffee beans contain from 5–12% of a fatty oil; the wax-free oil has an iodine value of about 100, a hydroxyl value about 23, and saponification value about 195, and contains about 12·6% of unsaponifiable matter (Schuette, Cowley and Chang, J. Amer. Chem. Soc. 1934, **56**, 2085; *cf.* Meyer and Eckert, Monatsh. 1910, **31**, 1227). The fatty acids consist chiefly of palmitic, linolic, and oleic acids, with smaller amounts of myristic, stearic, and arachidic acids; higher fatty acids (tetracosoic acid, the "carnaubic" acid of some writers) are present in the wax from the outside of the bean and are, therefore, found when the total ether-extract of the entire bean (saponification value 150–195, iodine value 80–100) is examined (*cf.* von Noël, Pharm. Zentr. 1929, **70**, 69; Heiduschka and Kuhn, J. pr. Chem. 1934, [ii], **139**, 269; Bengis and Anderson, J. Biol. Chem. 1934, **105**, 139; Bauer and Neu, Fette u. Seifen, 1938, **45**, 229). A phytosterol, m.p. 138–139°, and a substance, $C_{19}H_{26}O_3$ (m.p. 143–143·5°C.), termed "*kahweol*" (from the Arabic "qahweh," meaning coffee) have been separated from the unsaponifiable matter (Bengis and Anderson, J. Biol. Chem. 1932, **97**, 99; Dillingham and Thompson, Univ. Hawaii, Occas. Papers, 1934, No. 19; Bauer and Neu, *l.c.*). The oil is also stated to possess antirachitic activity (*cf.* von Noël and Dannmeyer, Strahlentherap. 1929, **32**, 769), which, like the characteristics of the oil, is not affected by the roasting of the coffee prior to extraction of the oil. Coffee oil does not appear to possess much technical interest at present, although a certain amount of the crude fat (including the wax) can be recovered as a by-product from the extracts obtained in the decaffeising of coffee by the solvent process; the recovery of the oil from coffee scheduled for destruction in Brazil has also been proposed. It is stated that during the War of 1914–1918 used coffee grounds were collected in Austria for the sake of the 12% of oil which was extracted therefrom (for soap-making ?) (*cf.* Fahrion, Z. angew. Chem. 1917, **30**, 125; Munk, Allgem. Oel- u. Fett-Ztg. 1932, **29**, 13), a practice which has recently been revived in Germany.

E. L.

COGNAC *v.* Brandy.

"COGWHEEL ORE" *v.* Bournonite.

COHENITE *v.* Cementite.

COHUNE NUT. The fruit of the cohune palm (*Attalea Cohune* Mart.), grown largely in Honduras. The nut is very similar in structure to the coconut, but is smaller. Its primary use is for the production of oil utilised largely for soap-boiling. The flesh of the nuts contains 4·5% of water, 65–71% of oil, and approximately 20% of protein. The principal protein is a globulin which may be extracted with brine and precipitated by addition of ammonium sulphate. Jones and Gersdorff give the nitrogen distribution of the globulin as:

	%
Amide-N	7·5
Humin-N	0·9
Cystine-N	0·5
Arginine-N	30·8
Histidine-N	2·6
Lysine-N	7·9
Amino-N of filtrate	47·9
Non-amino-N of filtrate	2·3

Tryptophan (0·65%) has also been detected (J. Biol. Chem. 1920, **45**, 57; 1924, **62**, 183).

A. G. Po.

COHUNE NUT OIL *v.* Coconut Oil Group. (this vol. p. 243*d*.)

COIR (or coconut fibre) is derived from the fibrous husk (mesocarp) of the fruit of the coconut palm (*Cocos nucifera* Linn.). This palm is distributed throughout the coastal regions of the tropics. It is cultivated extensively in India, Ceylon and Malaya, and is largely grown in the Philippine Islands and in South American countries. Some varieties of the palm are said to yield fibre of a finer quality than others; the quality is also influenced by the situation of the plantation, the fibre yielded by palms growing near the sea being finer than that from inland trees.

The fibrous material in its raw state consists of a mass of fibre strands of varying length associated with corky and other non-fibrous tissue. The best fibre is obtained from fruits that are gathered before they are quite ripe; as the nuts ripen the fibre becomes coarser and a longer period of steeping or retting is necessary, with the result that the coir acquires a dark colour.

In the preparation of coir by the native methods the husks are detached by striking the fruits on sharp spikes fixed firmly in the ground. The husks are immersed in pits containing brackish water, or in cages or wicker-work enclosures in backwaters, and left for several months. On modern estates the removal of the husks is effected by machinery, and the steeping is carried out in steam-heated tanks. When sufficiently softened, the husks are withdrawn from the water and are then beaten by hand with wooden mallets or passed through a crushing machine in order to free the fibres from the corky tissue. After leaving the crushing machine, the husk is passed into the extractor or breaking-down machine, in which it is completely disintegrated. The product is then dried and treated by a "willowing" machine to remove dust and other debris. The fibre is usually sorted by a combing or hackling process into grades of different lengths and qualities. The coarser and stiffer or "brush" fibre is used as bristles for brush-making, whilst the longer and finer "mat" or spinning fibre is employed for the manufacture of matting or cordage. The short fibre or tow is used in the form of curled fibre as a substitute for horse-hair as a stuffing material in upholstery, and the dust and refuse as a manure and for other gardening purposes.

Coir is composed of strong, elastic, reddish-brown filaments which are harsh to the touch and rather brittle. These filaments are thick in the middle and gradually taper towards the ends, the diameter in the widest part varying from 0·05 to 0·3 mm.; they are from 15 to 32 cm. long, and either round or elliptical in cross-section. The fibre is very resistant to the action of water and is so light as to float on it, and it is therefore of special service for the manufacture of ships' ropes.

The filaments are composed of fibro-vascular tissue consisting chiefly of very short, irregularly thickened fibres of uneven diameter; these ultimate fibres are about 0·4–1·0 mm. long and 12–20 μ in diameter.

The fibre substance consists of a highly lignified form of cellulose. On microchemical treatment with iodine and sulphuric acid, it gives a golden yellow colour, and with aniline sulphate an intense yellow colour; it is not attacked by Schweitzer's reagent.

E. G.

COKE MANUFACTURE AND THE RECOVERY OF BY-PRODUCTS.

Introduction.—Previous to the early nineties, practically the whole of British metallurgical coke was made in the old beehive oven, which, as will be seen from what follows, is a semi-combustion process, involving the loss of the whole of the gas and by-products, together with a portion of the possible coke yield. With the gradual disappearance of the old prejudices against coke made in by-product ovens, the latter and much more economical process began to assert itself, and in 1898, 1·25 million tons of coal were being carbonised in by-product coke ovens; in 1905 the quantity of coal so treated reached 3·31 million and in 1935 about 17 million tons. Meanwhile, the number of beehive ovens in operation had decreased from 16,037 in 1910 to 592 in 1935. According to figures published by the Coal Conservation Committee at the end of 1917, some 8,700 by-product ovens were in operation in Great Britain (of which 8,000 were fitted with benzol recovery arrangements) with a total carbonising capacity of 17·5 million tons of coal per annum. In 1917, 166,354 tons of ammonium sulphate were produced in British coke-oven plants. The practice of by-product recovery had become universal in Germany years ago; whilst in the United States the by-product plants, either building or in operation at the end of 1917, were capable of producing 24 million tons of coke per annum. In view of this rapid adoption of the by-product coking process in all these countries, the following article will be confined to a description of modern coking methods viewed chiefly from a by-product standpoint, with only a passing reference to the wasteful beehive process.

History of the By-Product Coking Process.—The earliest reference which we can find of any observation being made on coal as a source of by-products is that contained in the memoirs of Johann Joachim Becher, dating about the end of the seventeenth century; Becher states that he has found means for treating coal "so that it no longer smoakes nor stinks," and in doing so made a tar equal to the Swedish.

The use of coke in iron smelting became general within 50 years of Becher's discovery, and a French metallurgist, De Gensanne, describes a process working at Sulzbach near Saarbrucken prior to 1768, where coal was coked for iron smelting, tar being recovered as a by-product; Stahl is said to have been the inventor of this process, and he produced therefrom an "oil," bitumen, sal-ammoniac, and lamp-black.

In 1781 Archibald, Earl of Dundonald, was granted a patent for "allowing coals to burn or ignite without flaming, so by their own heat to throw off the tar or oils that they contain." Dundonald stated that the only method whereby tars could be obtained prior to his discovery was by a distillation in closed retorts, where the admission of external air was prevented and where other coals were required for heating besides the coal contained in the closed vessel. It is interesting to note that Dundonald was well aware of distillation in closed retorts, which is the basis of modern by-product coking methods, and it is also evident that his knowledge of closed retorts was 16 years previous to the introduction of coal gas for street and household illumination in 1797.

In 1838 Frederick Neville obtained protection for an invention which consisted in heating ordinary gas retorts by the waste heat from beehive coke ovens, the distilled gases from the retorts being passed through condensing and scrubbing appliances. William Newton, in 1852, introduced the use of an aspirator or pump for withdrawing the gases from coke ovens through condensers and scrubbers. Newton likewise mentions the use of acids for removing the ammonia from the gases. In 1860 W. H. Kingston patented a coke oven provided with external furnace, from which the heat evolved by the combustion of an auxiliary supply of coal was conducted round the oven through a system of flues; the evolved gases were passed through a series of pipes and condensing vessels for the recovery of the by-products. Kingston's patent is especially noteworthy, since he recognises that the true method for the recovery of by-products from coal lies in heating the coal in closed chambers, and not in chambers to which air is admitted.

With regard to Continental practice, in 1850 Pauwels and Dubouchet, and in 1862, Pernelot, introduced systems of carbonising coking coals in long rectangular chambers, heated from below by the regulated combustion of part of the gas in flues specially constructed under the floor, for the purposes of manufacturing metallurgical coke and removing tars, oils and ammonia. The Pernelot system was tried in the north of England in 1870, but the coke produced was too soft for metallurgical purposes.

In 1856 Knab erected a coal-distillation plant at Commentry, on the closed-retort system with bottom flues, but made no attempt to recover by-products. Later Knab was joined by Carvès, who (1866–1873) introduced improved methods of heating by side flues in addition to the bottom flues, thus obtaining a more even distribution of temperature and a quicker rate of carbonisation. Carvès likewise utilised the gases (from which the by-products had been extracted) in the side-wall flues, in addition to the auxiliary coal as employed by Knab. The Knab-Carvès ovens at Commentry gave the following results:

	%
Large coke	70·00
Breeze	1·50
Dust	2·50
Graphite	0·50
Tar	4·00
Ammoniacal liquor	9·00
Gas	10·58
Loss	1·92
	100·00

Further plant on the Carvès system were erected at Bessèges and Terre-Noire, near St. Etienne, between the years 1866 and 1873, and were still further improved; the Carvès ovens working at Bessèges in 1880 were built with carbonising chambers only 24 in. wide, to facilitate rapid heat penetration and quick carbonisation. In 1881 H. Simon of Manchester introduced a recuperator, whereby the air necessary for the combustion of the gas in the side-wall flues of the Carvès oven was preheated by the waste gases escaping from the flues, and thus the rate of carbonisation was still further increased, the combined work of the two investigators resulting in the well-known Simon-Carvès oven, which may be held to be the precursor of the modern by-product coking retort.

Following on the success of the Simon-Carvès process, other coke-oven patents were filed, viz. Semet-Solvay, 1880; Hüssener, 1881; Lürmann, 1882; Otto and Brunck, 1883; but although development was rapid on the Continent, little was done in this country before the nineties, owing to the prejudice of iron smelters against by-product coke; that this prejudice has now disappeared will be seen from the rapid adoption of the process, indicated by the figures at the beginning of this article. The by-product coking plant which have generally found acceptance in this country are the Otto-Hilgenstock, Simon-Carvès, Koppers, Semet-Solvay, Simplex, Coppée, and Hüssener.

NON-BY-PRODUCT AND BY-PRODUCT OVENS COMPARED.—Prior to the establishment of the by-product coking process, the type of oven universally employed was that known as the beehive. This oven (Fig. 1) consists of a fireclay chamber, beehive shape in elevation and circular in plan, provided with a loose brick charging door at ground level, and with an exit flue in its crown for carrying the waste gases to the chimney. The coal is charged into the oven by spades, through the charging door, to a height of 2 ft. 6 in. to 3 ft., is then ignited, and the charging door bricked up and plastered, a small hole 6 in. square being left for the admission of air. The upper layer of the coal burns and sets up distillation of the under layers, the evolved gases passing upwards and burning in the dome of the oven, with the air drawn in at the door. The dome is thus soon heated up to a high temperature, and by radiation powerfully assists in carbonising the charge of coal below. This operation of distillation and immediate combustion proceeds until the whole of the volatile constituents of the coal have been evolved, which for a 10-ton charge occupies 70 hours. The coke is then quenched with water and withdrawn by rakes.

It will be seen that by this process, the whole of the volatile products, that is to say, volatile hydrocarbons and ammonia together with the permanent gases, are burned immediately they are evolved within the coking chambers itself ; further that it is not possible so to regulate the combustion of these gases without burning a portion of the coke in addition ; in actual practice, from 15 to 20% of the coke is burned to waste. For the reason, too, that the coke is quenched inside the oven, the temperature of the latter is lowered, so that before the next charge can be coked, considerable expenditure of heat is necessary to raise the oven to coking temperature. The removal of the coke by hand-rakes is also tedious and expensive.

With the object of overcoming the main drawbacks of the beehive oven, Coppée introduced a non-by-product retort of rectangular form, from which the coke could be discharged *en bloc* by a ramming machine and quenched outside the oven, thus expediting the operation and greatly increasing the yield. In Coppée's oven (Fig. 2) the gases evolved from the coal are drawn into flues in the side walls where they are burned, and in this way combustion within the coking chamber and loss of coke, as occur in the beehive oven, is avoided.

The by-product retort (Fig. 3) is built on the same lines as the Coppée, that is to say, it is a rectangular chamber heated by flues in the side walls, and the coke is discharged by a ramming machine; the essential point of difference lies in the fact that in the Coppée the whole of the gases containing the by-products are drawn immediately they are evolved into the side-wall heating flues, where they are burned ; in the by-product retort, the gases and products are drawn from the oven through cooling and washing plant for the recovery of the tars, ammonia, and benzol, and the permanent gas only is burned in the flues after the said products have been extracted. In the Coppée, the whole of the permanent gas is burned in the heating flues ; in the by-product oven, only one-half to two-thirds of the gas is utilised in the flues, the remainder being available for heating or power purposes.

The diagrams (Figs. 1, 2, and 3) clearly illustrate the essential differences in the three types of oven discussed above.

It will be seen, therefore, that in addition to obtaining the theoretical coke yield, and a large output, the by-product retort yields valuable by-products and a considerable yield of power or heating gas. The average yields (calculated upon 100 parts of *dry* coal) of coke and by-products obtainable from British coking coals of different origin by the most up-to-date methods, are approximately as follows :

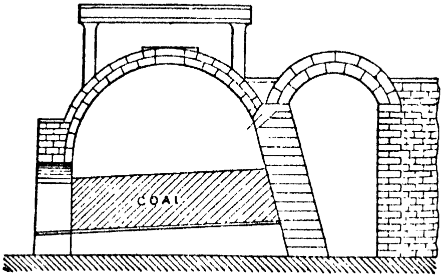


FIG. 1.—BEEHIVE.

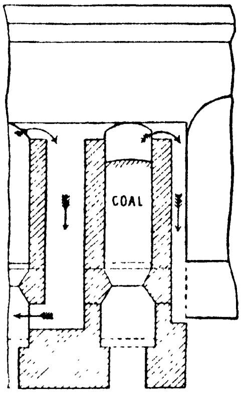


FIG. 2.—COPPÉE.

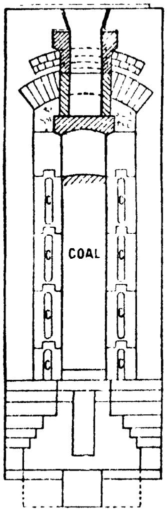


FIG. 3.—BY-PRODUCT RETORT.

Origin.	Coke.	Anhyd. tar.	Crude benzol.	Ammonium sulphate.
Durham . .	75·0	3·85	0·93	1·16
South Yorkshire	70·0	3·62	1·37	1·35
Lancashire .	70·0	3·50	1·20	1·25
South Wales .	80·0	2·62	0·60	0·95
Scotland . .	68·0	3·25	0·70	1·00

COKE OVEN DESIGN AND CONSTRUCTION.—A modern by-product coke oven is a rectangular chamber from 40 to 45 ft. long, 12 to 20 ft. high, and from 14 to 20 ins. wide. It is closed at each end by a cast iron or steel door with firebrick lining, which is lifted by a small crane whenever the contents of the oven are to be discharged. There are three or four holes in the roof through which the coal is charged into the oven from an electrically-driven charging lorry which runs on rails along the battery of ovens. At one or both ends of the oven there is an iron "ascension pipe," through which the gas and volatile matter expelled from the coal during the carbonising period are led into the "hydraulic main" running along the whole battery of ovens, much as in gas-works practice.

The ovens and heating flues are usually constructed of silica brick, consisting of silica 92 to 96%, alumina 2 to 3%, lime 1·3 to 2·5%; such bricks are more stable at high temperatures and have a higher heat conductivity than the more aluminous bricks formerly employed; consequently, higher flue temperatures can be carried, as a result of which the speed of coking is increased while the heat economy of the system is improved, leading to a decrease in the quantity of gas required to heat the ovens.

The charge of such an oven is from 15 to 25 tons, and the coking time from 12 to 22 hours, equivalent to a throughput of from 25 to 30 tons of coal per day.

Coke ovens are built in batteries of from 25 to 160 units; they are heated by gas which is burnt in flues between the ovens so that the charge is carbonised by being heated from either side. The design of the heating flues varies much, but practically all modern coke ovens have vertical heating flues, the underlying principles being to economise as far as possible the amount of gas required to effect the carbonisation, and to enable the greatest possible area of oven wall to be uniformly heated. The gas used for heating may be either part of the coke-oven gas after it has been passed through the by-product plant for recovery of tar, ammonia, benzol, etc., or provision may be made for heating the ovens by low-grade fuels such as producer or blast-furnace gas. In any case, however, the air required for combustion is pre-heated before it enters the combustion flues at the expense of part of the sensible heat in the burnt gases passing from the ovens. Where producer or blast-furnace gas is used for heating, such gas is also pre-heated in the same way as the air.

Generally, top charging is practised, cleaned slack coal being simply run in through the charging holes in the roof of the oven, the charge afterwards being levelled by means of a small ram above the main ram which is introduced through a hole near the top of one of the end doors of the oven. Where weakly caking coals are carbonised, the charge is sometimes "stamped" before being introduced into the oven. In such cases, the crushed coal is compressed by a mechanical stamping machine in a wrought steel box slightly less in size than the oven chamber, and pushed *en bloc* into the oven as a solid cartridge through the front doorway on the movable bottom of the box which forms the charging peel. At the end of the carbonising period the coke is discharged from the ovens by an electrically driven ram and either quenched by water as it emerges from the ovens or else at a remote quenching station such as will be described later. A good deal of attention has, of recent years, been devoted to dry-cooling of coke with a view to improving its quality and at the same time recovering part of the sensible heat, but wet cooling is still the general practice.

As an example of modern coke-oven construction, a short description of the Becker oven is given.

The Becker Coke Oven.—This oven, which is illustrated in Figs. 4 and 5, is of the vertical flue type and the heating system is arranged so that either lean (blast-furnace or producer) gas or rich (coke-oven) gas may be used. Each oven has a series of vertical flues on either side, under each of which two regenerators are built.

When employing blast-furnace or producer gas for heating, air passes up one of the two regenerators and gas up the other. Both the air and the gas enter their respective regenerators from both sides of the oven at the same time; on leaving the top of the regenerators they enter the bottom of the heating flues so that the air and gas come together with streamline effect and the combustion zone is evenly distributed throughout the length of the vertical flues. The products of combustion are collected from the top of each four or five vertical flues and carried over the top of the oven by means of cross-over flues (Fig. 4), of which there are six to each alternate oven, the intermediate ones not requiring any, as may be seen from the diagram.

From these flues the waste gases are distributed to an equal number of vertical flues on the other side of the oven exactly opposite the flues up which they have travelled. They then pass down these flues and into the regenerators immediately below, through which they pass to the waste gas flues, giving up a portion of their sensible heat to the chequer work in transit.

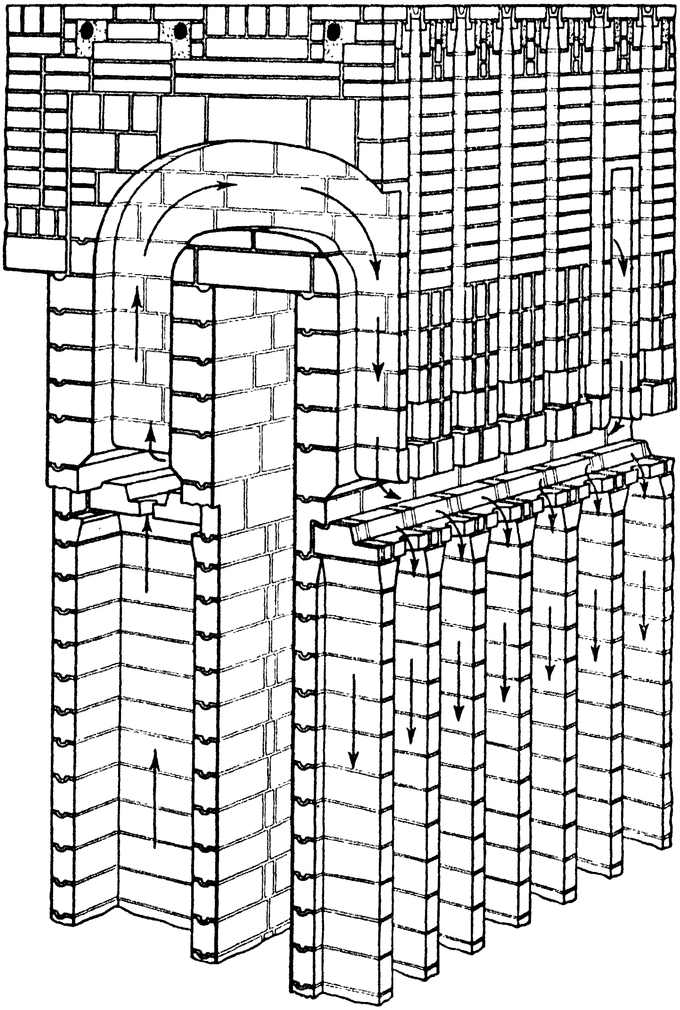
At the end of a pre-determined period (from 20 to 30 minutes) the direction of flow of gas and air is automatically reversed, so that the regenerators which have been heated by the waste gases are used to heat the air and fuel gas, while the relatively cool regenerators are heated up. The regenerators are so arranged that those in which gas is being heated are never adjacent to those in which waste gas is flowing, and leakage of fuel into waste gas is therefore impossible.

When rich gas is employed as the heating medium, air passes up all the regenerators and cold coke-oven gas is delivered through a horizontal gas conduit carried in the brickwork between the top of the regenerators and the bottom of the heating flues. From these conduits the gas passes by means of a calibrated nozzle and vertical duct into the bottom of each vertical flue where it mixes with the preheated air coming from the regenerators. The flow of gases from this point is the same as when blast-furnace gas is used.

QUENCHING AND COOLING THE COKE.—A common system of quenching the coke is to spray it with water under pressure while it passes through a cage of pipes on emerging from the oven. The coke then falls on to an inclined coke wharf where it "steams off" and cools and where any hot spots are quenched by water from a hose.

Where dry cooling is practised, the red hot coke is delivered into a firebrick chamber through which inert gases (derived from the air introduced with the coke) are circulated in closed circuit through the coke and over the tubes of a boiler, by which means it is claimed that some 1,000 lb. of steam (from and at 212°F.) may be raised per ton of coke.

The practice of remote quenching is now coming into favour ; in this process, the coke is discharged into a car which is slowly moved across the end of the oven, thus spreading the coke out as a thin layer. The car is rapidly pushed to the quenching station, usually a tower (serving also as a chimney to carry away the large volume of steam produced), where a predetermined quantity of cold water (generally about 3 tons per ton of coke) is sprayed under pressure on the coke. The surplus water is allowed to drain away into a settling pond, while the coke, after draining, is allowed to slide from the car on to the wharf where it steams off and cools finally ; by this process uniformity of moisture content is secured, the final moisture being maintained as low as 2%.

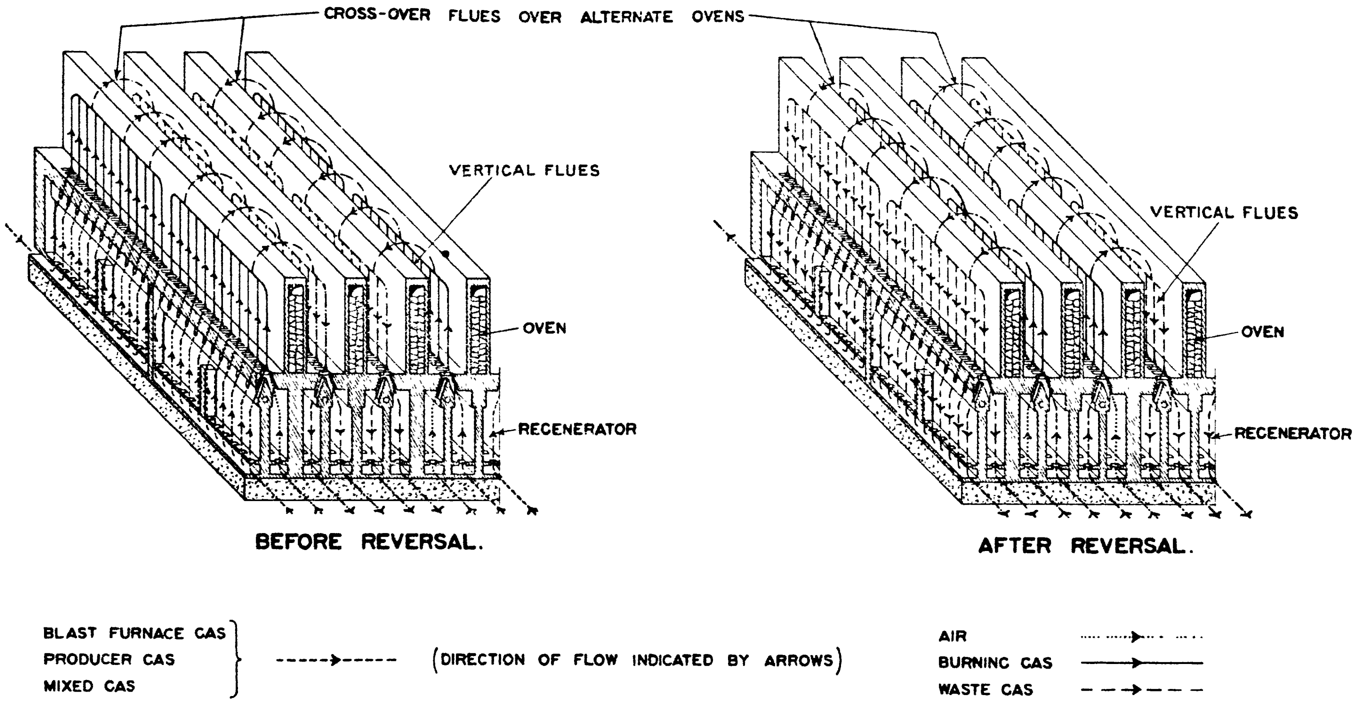


[*By courtesy of Messrs. Woodall-Duckham, Ltd.*

FIG. 4.—THE BECKER COKE OVEN. SHOWING THE CROSS-OVER FLUE.

RECOVERY OF BY-PRODUCTS.—Three general systems are in operation, the Indirect, the Direct, and the Semi-Direct. The first of these is similar to that employed in gasworks: tar and ammonia liquor are condensed, while the last traces of tar are scrubbed from the gas in a tar extractor, after which the residue of the ammonia is removed by washing the gas with water. In this process all the ammonia is obtained in the form of an aqueous solution which must be further treated in order to produce ammonium salts.

In coke-oven practice, direct and semi-direct recovery systems are more frequently employed ; they differ from the indirect process in that the ammonia is either directly recovered as



[*By courtesy of Messrs. Woodall-Duckham, Ltd.*

Fig. 5.—The Becker Coke Oven. Showing the Method of Heating.

ammonium sulphate without the condensation of liquor, or part of the ammonia is directly recovered as sulphate and part as an aqueous solution which must be distilled for recovery of the ammonia.

The Otto Direct Recovery Process.—This process, which is represented diagrammatically in Figs. 6 and 7, consists in extracting all the tar from the hot gas above its dew-point, and then forcing the tar-free gas, without any re-heating, through a saturator in the main circuit containing dilute sulphuric acid, under conditions such that the natural heat in the gas, aided by the exothermic interaction of the ammonia and sulphuric acid, keeps the volume of the absorbing liquor constant and the separation of ammonium sulphate proceeds continuously.

Such a method of "direct recovery" entirely dispenses with the use of water coolers, ammonia scrubbers, lime mixers, ammoniacal liquor stills, and waste liquor tanks, reduces the loss of ammonia to a minimum, economises space and labour, and avoids the making of deleterious effluents which were formerly a serious source of trouble.

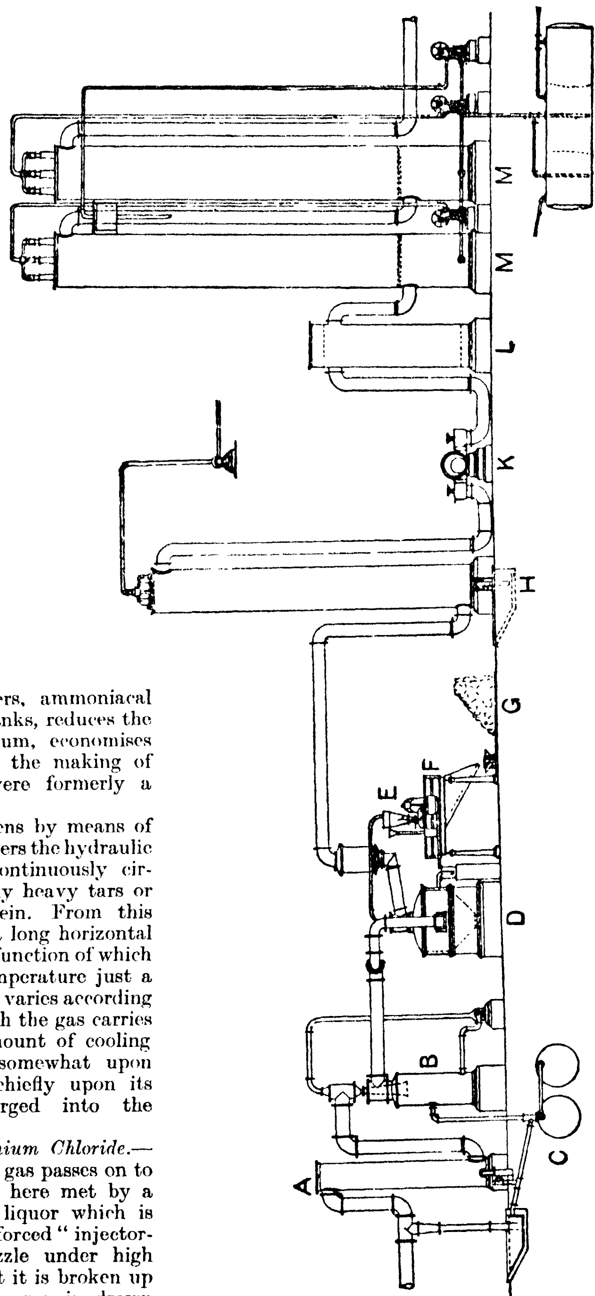


FIG. 6.—OTTO DIRECT RECOVERY PROCESS.

The crude gas leaves the ovens by means of the usual ascension pipes and enters the hydraulic main through which tar is continuously circulated, in order to remove any heavy tars or pitchy matter deposited therein. From this point the gas travels through a long horizontal overhead "air cooler," the real function of which is to cool the hot gas to a temperature just a little above its dew-point, which varies according to the amount of moisture which the gas carries over from the ovens. The amount of cooling necessary therefore depends somewhat upon the nature of the coal, but chiefly upon its moisture content when charged into the ovens.

Recovery of Tar and Ammonium Chloride.—After leaving the air cooler, the gas passes on to the "tar extractor," B. It is here met by a large volume of hot tar and liquor which is pumped into the apparatus and forced "injector-wise" through a narrow nozzle under high pressure, in such a manner that it is broken up into a fine spray. The crude gas is drawn into the apparatus by this "injector" action, and the sprayed tar and liquor dash against the small tar vesicles contained in the gas. This mechanical spraying of the gas, together with the solvent action of the washing medium, results in the complete removal of tar, including tar fog, from the gas, which passes out of the extractor in a perfectly clean condition. Also, it should be noted that if a "salty" coal is being carbonised, so that the crude gas contains ammonium chloride, the latter may be removed at the tar sprays as a fairly strong aqueous solution. Indeed, "fixed ammonia" generally may be removed at this point provided the temperature conditions are such as will allow of the condensation of a small amount of liquor in the apparatus. From this the importance of a perfect control of the temperature of the gas, both in entering and leaving the apparatus, will be understood. The tar extracted from the gas overflows into the tar deposit tank, C, which also serves to recover any tars which separate in the long "air cooler," A, already referred to.

Recovery of Ammonia.—The tar-free gas, which still contains the free ammonia, benzol, and nearly the whole of the naphthalene and water vapour, passes onward, at a temperature (say between 65° and 75°C.) so regulated as to be near to (but not below) its dew-point, into the large enclosed "saturator," D, containing a hot saturated solution of ammonium sulphate *plus* an excess of sulphuric acid. In this apparatus, which is lead-lined and cased in a cast-iron framework, the gas is divided into a very large number of small streams, and, under the suction of an exhauster, K, applied at a point further along the system, it is drawn through the seal of the acid liquor, whereby all the ammonia is removed, and precipitated as sulphate in the coned bottom of the saturator. The exothermic reaction serves to keep the temperature of the gas above the dew-point, so that no condensation of steam occurs in the saturator. The salt is mechanically and continuously ejected from the apparatus by means of compressed air, together with a certain amount of solution, into the cone-shaped receiver, E. The ammonium sulphate crystals settle to the bottom of this receiver, while the hot mother liquor overflows from the top and finds its way back into the saturator. When this cone-shaped receiver is full of the crystallised sulphate it is passed into a centrifugal dryer, F.

In this machine the sulphate is made thoroughly dry in about three minutes, the mother liquor thus extracted mixing with the above-mentioned mother liquor and with it flows back into the saturator, while the dried sulphate of ammonia is dropped through the bottom of the centrifugal machine, sufficiently dry to be immediately bagged and shipped or put into stock, as shown at G in the diagram.

Recovery of Naphthalene.—The gas from the saturator, which is now free from both ammonia and tar, but still contains the benzol, moisture, and naphthalene, passes through a lead-lined catch pot (seen as an enlargement in the gas main, whose function is to prevent any acid spray being carried over from the saturator) and on to the naphthalene extractor and spray cooling tower, H. This tower is quite devoid of any filling, but at the top there are several jets through which cold water is sprayed at high pressure. The action of this mass of finely-divided cold water beating suddenly on to the hot gas produces a rapid chill, which, together with the concussion brought about by the water, precipitates and washes out practically all the naphthalene, which flows away along with the water into a catch tank below. The naphthalene is filtered off while the water can be either allowed to flow away or re-cooled and used over again continuously, as circumstances permit. This tower also serves to cool the gases. It is necessary to extract the naphthalene, otherwise it would pass on to the benzol scrubbers, where it would be dissolved

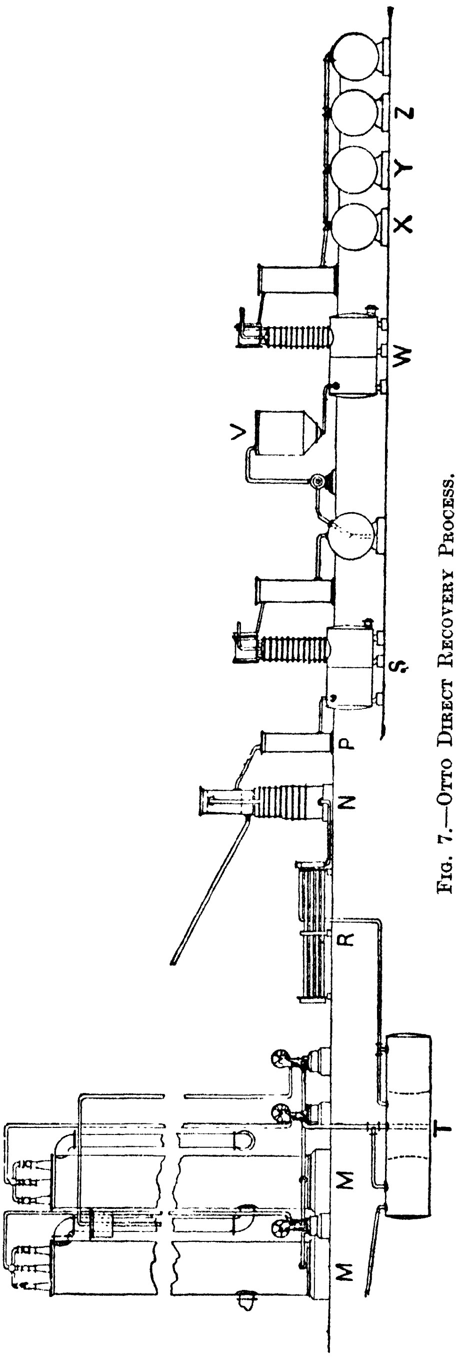


FIG. 7.—OTTO DIRECT RECOVERY PROCESS.

by the wash oil, which would very soon become saturated with naphthalene and rendered useless for the purpose of collecting benzol. The naphthalene thus extracted is of a pale yellow colour, and is readily sold at a price which more than pays the cost of running this part of the plant.

Recovery of Benzols.—The gas now being cool, but still containing the benzol, passes through the exhauster, K, and a second water cooler, L, which takes out the last traces of naphthalene, and thence to the benzol scrubbers, MM, which vary in number according to the size of the plant. These scrubbers are from about 50 ft. to 70 ft. high, the lower portion forming a reservoir for the circulating benzol wash oil, and the remaining portion being filled with wooden grids. Benzol wash oil is constantly circulated downward over these grids, the gas having to pass upward through them. By this means the gas is brought into very intimate contact with the oil, with the resulting absorption of the benzol. After leaving these scrubbers the gas passes either wholly back to the ovens, or in the case of regenerative ovens, about one-half of it returns to the ovens, and the other half is used either for firing boilers, town lighting, operating gas engines, or other purpose.

According to E. Bury (Trans. Inst. Min. Eng. 1911, p. 537), the following temperatures were observed in a plant at New Brancepeth Colliery (Co. Durham):

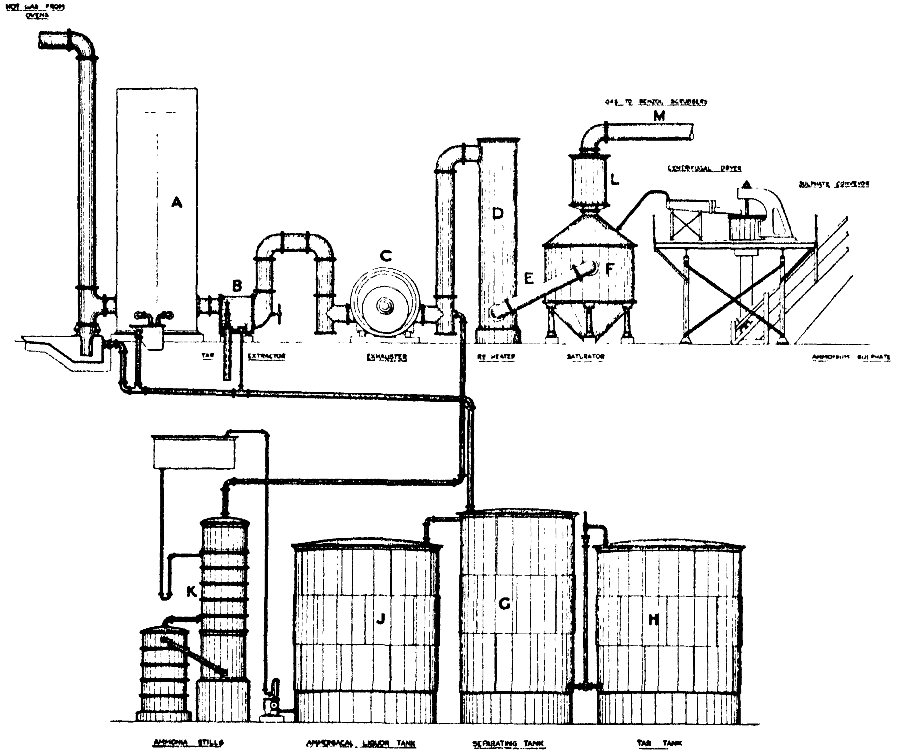


Fig. 8.—The Koppers Semi-Direct Recovery Process.

	°C.
Hydraulic main	225
Before tar extraction	86
After tar extraction	58
In saturator	67
After saturator	58
After exhauster	66

Distillation and Rectification of Benzols.—The "wash oil" containing the benzols in solution is sent to the continuous crude benzol still, N (Fig. 7), where, after being pre-heated by the hot vapours coming away from the still, it passes downward over a series of trays. Dry steam at about 100 lb. pressure, reduced, however, at the still to 10 lb. pressure, is delivered into the bottom of the apparatus, and passing upwards bubbles through the wash oil, liberating the benzol hydrocarbons which it carries over into the condenser, P. Here the steam and benzols are condensed, and the condensed water and oil separated. The crude benzol then either passes into a storage tank, or (if its rectification is to be carried out) into the "primary rectifying still," S. The debenzolised "wash oil" leaving the crude benzol still is passed through the refrigerator, R, whence, after being cooled to the atmospheric temperature, it is sent into the "oil storage tank," T, and from there it is used again in the benzol scrubbers.

The crude benzol is first of all fractionally distilled in the primary rectifying still, S, 3,000 to 5,000 gallons capacity and intermittent in its working, in which it is heated under reduced pressure by means of steam coils, and, with the aid of a long dephlegmating column, it is separated into:

(1) Crude 90% Benzol.
(2) Crude 90% Toluol.
(3) Crude 90% Xylol.
(4) Crude 90% Solvent Naphtha.

Each of these fractions is separately condensed and pumped into a large vessel, V, termed the agitator, where it is successively treated with (*a*) pure strong sulphuric acid, and (*b*) a solution of caustic soda, in order to remove all resinous, basic, or acidic substances. Each of the "washed" fractions is finally refractionated under reduced pressure in the "secondary rectifying still," W, and the re-distilled resulting fractions, after condensation, are sent forward into their respective storage tanks, XYZ, ready for transport.

Other firms (*e.g.*, the Simon-Carvés, the Collin, and the Simplex Companies) have also adopted efficient "direct recovery" processes, on much the same lines as the Otto process just described, the chief difference between them being in the precise mechanical arrangement for the removal of tar and tar fog from the hot gas before it enters the saturator where the ammonia is absorbed.

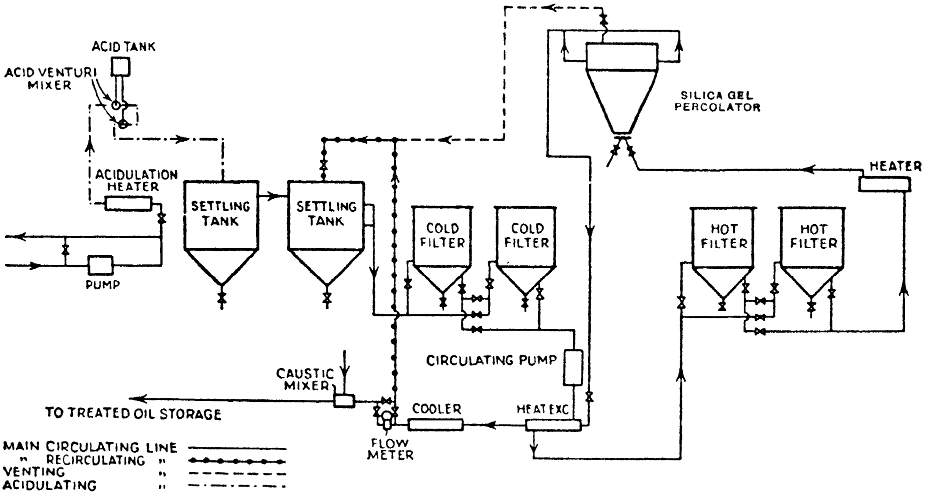


FIG. 9.—DIAGRAM OF PLANT FOR THE REFINING OF BENZOL BY MEANS OF SILICA GEL.

The Koppers' Semi-Direct Recovery Process.—In this process (illustrated in Fig. 8), the hot gases from the ovens are first cooled approximately to air-temperature in the primary coolers, A, where the tar and water vapours are condensed. The gases are then drawn by the exhauster, C, through the tar-extractor, B, where the last traces of tar fog are mechanically removed. The tar-free gases are next heated to about 50° to 60°C., in the re-heater D, by means of exhaust steam obtained from the engines used in the recovery plant, and are then brought into contact with sulphuric acid in the saturator, F, where the ammonia is removed as ammonium sulphate.

The tar and ammonia liquor which are extracted in the primary cooler and tar extractor are collected and delivered into the decantation tank, G, where separation takes place, the tar and liquor being separately run into the storage tanks H and J. The liquor is continuously pumped into the ammonia still, K, where the free and fixed ammonia are driven off by steam and lime. The vapours from the still are returned into the gas-stream and pass with it into the saturator.

After leaving the saturator, the gases pass through the acid-separator, L, where any acid spray carried forward from the saturator is removed, and thence are conducted by the main, M, to the benzol-recovery plant which operates on the same general lines as that already described.

As an alternative to the oil-washing process, the recovery and refining of benzol by solid adsorbents (silica gel or activated carbon) has been developed. For the use of activated charcoal for this purpose, *see* end of article. E. C. Williams (Proc. Chem. Eng. Group, S.C.I. 1924, **6**, [A], 95–114) discussed the principles of the recovery of benzol by silica gel and described an experimental plant designed by the Silica Gel Corporation. This process does not yet appear to be operating on the large scale, the main difficulty being the serious wastage of the gel; silica gel, however, is employed in the refining of benzol, and this process is dealt with below.

Benzol Refining by Silica Gel.—The silica gel process for benzol refining is primarily catalytic, polymerisation of the gum-forming impurities being initiated by acid treatment, the gums are then deposited on the surface of silica gel, where they act as catalysts to polymerise the remaining unsaturated hydrocarbons. The crude benzol is pumped through a tubular steam heater (the "acidulation heater" in Fig. 9, p. 267) to raise its temperature to about 40°C. Thence it flows through two Venturi meters; while passing the first, 0·1% of concentrated sulphuric acid is added to dry the benzol, and at the second meter, 0·2% to initiate polymerisation. After passing through two settling tanks where a small amount of sludge is drawn off, the acidulated benzol passes through a coke filter, and is then pumped *via* a heat exchanger, where it is heated by hot benzol from the silica gel percolator, and is afterwards filtered while hot through the "hot coke filter." After being heated to about 150°C. (under pressure sufficient to maintain it in liquid phase), the benzol passes upwards through the conical silica gel percolator where polymerisation and removal of gumming constituents are completed, it passes through the heat exchanger counter-current to the benzol from the circulating pump, through a cooler, and flow meter, and finally, after treatment with caustic soda to remove acidity, to storage. After the silica gel percolator has been used to treat 1,500 times its own weight of benzol, it is removed for re-activation, and replaced by a freshly re-activated charge.

In dealing with the subject of by-product recovery, mention should be made of the fact that the rapid development of the synthetic ammonia industry has led to a fall in the price of ammonium sulphate which has rendered ammonia recovery from coke-oven gas so much less profitable than formerly that in some cases it has been abandoned. In Table I the production of ammonium sulphate and ammonia liquor at coke-oven plants in the United Kingdom in 1924 and 1930 are compared.

The quality of ammonium sulphate now marketed is higher than that before the War, the salt being neutralised and dried before being placed in storage. The specification of the British Sulphate of Ammonia Federation demands that the salt should fulfil the following requirements: Nitrogen content to be not less than 20·60%; free acidity (calculated as H_2SO_4) not greater than 0·025%; and moisture not over 0·20% (±0·05%).

TABLE I.—PRODUCTION OF AMMONIUM SULPHATE AND AMMONIA LIQUOR AT COKE OVEN PLANTS IN THE UNITED KINGDOM.

	1924.	1930.
Total coal carbonised in by-product ovens, million tons	17·23	16·51
Ammonium sulphate produced, tons	186,200	173,100
Sulphate produced per ton of coal, lb.	24·2	23·5
Ammonia liquor produced, tons	12,700	5,800

THE UTILISATION OF COKE-OVEN GAS.—The similarity in composition of the gas obtained from a given coal when carbonised at high temperatures either in a coke-oven of the type already described or in a vertical gas-retort (as illustrated in Table II) is such that the fields of utility of coal- and coke-oven gases are likely to be the same.

TABLE II.—COMPOSITIONS OF COKE-OVEN AND VERTICAL-RETORT GASES BEFORE BENZOL RECOVERY.

	Coke-oven gas. Mixture of S. Yorkshire and Derbyshire coals carbonised in Becker ovens.	Vertical retort gas. Mitchell Main ga s nuts carbonised in Glover-West vertical retorts.
Percentage:		
CO_2 . . .	2·2	0·8
CO	6·8	7·4
C_nH_m . . .	3·0	2·2
CH_4 . . .	28·2	29·05
H_2	52·6	52·0
O_2	0·8	0·6
N_2	6·4	7·95
Calorific value (B.Th.U.) per cu. ft. (gross at 15°C.) and 760 mm. .	553·4	554·0

Debenzolised Gas.—The amount of benzol vapours included among the unsaturated hydrocarbons, C_nH_m, in the above table would be approximately 1% in each case, and the effect of removing them would be to reduce the calorific value of the gas by from 5 to 10%. The average percentage composition of the "debenzolised" gas from typical Durham and South Yorkshire coking coals is somewhat as follows:

	CO_2	CO	C_nH_m	CH_4	H_2	N_2	Calorific values (B.Th.U.) per cu. ft. at 15°C. and 760 mm.
Durham	2·5	6·5	2·0	25·0	55·0	9·5	484·6 gross 425·5 net
S. Yorks.	2·4	5·6	2·0	26·4	54·6	9·1	493·6 gross 434·2 net

Amount of Surplus Gas.—Taking the country as a whole, and assuming that the whole of the 17·4 million tons of coal carbonised in 1935 for metallurgical coke was dealt with in regenerative ovens, the *net* calorific value represented by the surplus gas (at 5,500 cu. ft. per ton) available for outside purposes might have been about 47,300 therms per hour, day and night, or sufficient to generate about 490,000 B.H.P. continuously in internal combustion engines.

The most effective utilisation of such a huge surplus of energy is a matter of the highest importance to the nation, and there is no doubt that a good deal of the coke-oven gas available from existing plants is not being used to the best advantage.

Table III, taken from the reports of the Secretary of Mines, shows the make of coke-oven gas and how it was actually used during the period 1932 to 1935. In 1935 the average gas production was 10,870 cu. ft. per ton of coal, of which 59·5% was used for heating the ovens, while a further 23·5% was used for other purposes by the oven owners, for steam raising or on steel works where the ovens and steel works were under common management. About 11% was sold to gas companies and 3·5% to other undertakings, leaving a balance of about 2½% unaccounted for.

TABLE III.—BY-PRODUCT COKE-OVEN GAS PRODUCTION AND DISPOSAL.

Year.	1932.	1933.	1934.	1935.	Cu. ft. per ton of coal, 1935.
	Million cu. ft.				
Total produced	124,230	137,492	177,070	185,558	10,870
Used by Oven Owners.					
For heating ovens	89,092	81,269	106,519	110,236	6,460
For other purposes		31,790	40,146	43,731	2,560
Sold to					
Gas undertakings	15,480	15,941	18,052	20,474	1,200
Other undertakings	15,994	6,240	8,276	6,327	370
Balance	3,732	2,251	4,078	4,791	280

In normal times by far the greater part of the coke manufactured outside gasworks is for metallurgical purposes, and chiefly for iron-smelting. In cases where blast furnaces are attached to steel-works, the utmost fuel economy may be achieved by concentrating coke ovens, blast furnaces, steel-furnaces, and rolling mills as a self-contained plant on one site so that combined surpluses of coke-oven and blast-furnace gases may be utilised, thus making it possible to produce finished steel sections from the ore with no more fuel than the coal necessary to furnish the coke required in the blast furnace. In such cases there is usually no surplus coke-oven gas available for outside purposes except at week-ends, when the steel-works and rolling mills are shut down.

Such considerations do not, however, apply to independent blast furnace plants producing foundry iron (*e.g.* in the Midlands) or to high-grade steel-works (*e.g.* the Sheffield area) unattached to blast furnaces. In such areas the coke-oven plants are usually situated at the collieries, and large surpluses of gas are available for outside purposes. Thus it has been estimated that in 1928 within the area comprising South and West Yorkshire, Lancashire, Derbyshire, Cheshire, Notts, Lincolnshire, Staffordshire, Leicester and Warwickshire, there were available for "outside" purposes about 10,000 million cu. ft. of coke-oven gas of an average calorific value 500 B.Th.U. per cu. ft., of which about 4,200 million cu. ft. were sold to gas undertakings, and another 2,150 million cu. ft. to other undertakings. Moreover, with new coking plants then contemplated, it was considered that the total available surplus gas within the area might soon amount to as much as about 22,500 million cu. ft. per annum. Such a prospect, being subject to fluctuations in the activity of the iron and steel industry, is therefore to some extent doubtful, which is a serious drawback from the point of view of public distribution to undertakings outside iron and steel works.

Considerable developments have recently taken place in European countries, and particularly Germany, in regard to the pooling and distribution over large areas of such surplus coke-oven gas ; and the question arises whether or not some such schemes would be equally practicable in certain areas of Great Britain, seeing that nowadays there would be no technical difficulties to overcome. Thus, for example, at the end of 1929 in Germany the Ruhr Gas A.-G. (established in 1926) owned 286 miles of welded steel mains, with a further 330 miles under construction or contemplated, and in 1930 distributed some 21,000 million cu. ft. of coke-oven gas ; moreover, in 1929, about one-third of the total gas consumed (*i.e.* from gasworks and coke ovens) in Germany was derived from the Ruhr coke ovens. The gas is guaranteed free from tar and H_2S, the maximum permissible content of NH_3 being fixed at 0·87 g. and of naphthalene at 4·37 g. per 100 cu. ft. The price delivered to gas companies is usually based on a sliding scale according to the price of coal (*e.g.* to Hanover at the equivalent of 11·6*d.* per 1,000 cu. ft. up to 1,765 million cu. ft. per annum, and at 10·6*d.* per 1,000 cu. ft. for consumption exceeding 2,472 million cu. ft. per annum, when the price of coking coal is equivalent to 18*s.* 9*d.* per ton), but to industrial establishments the price is equivalent to 10*d.* per 1,000 cu. ft.

In 1930 a Departmental Committee of the Board of Trade was appointed to inquire into the technical and economic aspects of an area gas supply comprising the afore-mentioned counties in England, and, after hearing much evidence, reported that while circumstances would not warrant the construction of elaborate and expensive systems of trunk mains over the whole area, and are not yet favourable for such network either in Lancashire or West Yorkshire, the iron and steel industry around Sheffield and Rotherham offers a good market for all the surplus coke-oven gas likely to be available in the near future if it could be supplied at an average price of 2*d.* per therm (=say 10*d.* per 1,000 cu. ft.). Accordingly they recommended the adoption of a scheme for such restricted area embodying the following conditions (*inter alia*); (i) To collect gas from 19 coke-oven plants and to take a maximum volume of 80 million cu. ft. of gas per day, the flow of gas to be uniform throughout the 24 hours of the day; (ii) the gas to be purified at the coke ovens before delivery into the network; (iii) the compressor plants to be installed at the coke ovens and their cost and the cost of operation to be met by the coke-oven owners, such costs being covered by them in their price of gas; (iv) the pressures to be used to vary from 2·7 lb. to 8·2 lb. per sq. in., when the mains are carrying up to 40 million cu. ft. per day, and from 4·9 lb. to 22 lb., when they are carrying up to 80 million cu. ft. per day; (v) the length of the mains to be approximately 73½ miles, and to be of steel of medium weight varying from 6 in. to 30 in. in diameter with hessian cloth and with bitumen coating, and laid in roads, receiving 3 ft. cover, at an estimated capital cost of approximately £537,900; (vi) the cost of distribution (excluding compression) to vary from 1·33*d.* per 1,000 cu. ft. (0·25*d.* per therm) with a volume of 40 million cu. ft. per day to 0·66*d.* per 1,000 cu. ft. (0·13*d.* per therm) with a volume of 80 million cu. ft. per day.

It was further considered that the conditions of gas supply in Germany (where town's gasworks production is less than half that in Great Britain, and the consumption per head of population about 1,800 cu. ft. per annum as compared with over 6,000 cu. ft. in Great Britain) " are so dissimilar to those in this country that it does not follow that long-distance transmission of gas can be introduced into Great Britain on the German model."

Among other directions in which the surplus gases can be utilised to good advantage may be mentioned :

For Steam Raising and Power Purposes.—By burning the gases in the tubes of a Bonecourt Boiler, on the principle of " surface combustion," it is possible to transform 92% of the *net* heat of combustion into the energy of steam which can be either (*a*) converted into mechanical power by means of a steam turbine, or (*b*) used for evaporative purposes in connection with chemical operations. Or, power may be generated from the gases by means of large internal combustion engines, with a thermal efficiency of, say, from 20 to 25% (*i.e.* from *net* calorific value of the gas to B.H.P. at the engine). And by suitable combinations of either (*c*) boilers, turbines, and dynamos, or (*d*) gas engines and dynamos, electrical energy can be generated at a very low cost. Many collieries now generate from their surplus coke-oven gases (or waste heat) sufficient power to meet all the requirements of the mine. Others, again, sell their surplus gas (or waste heat) to a power company, which converts it into electric energy which is distributed for public consumption over a wide area, as in the North-East Coast Power Scheme.

If no power company, or group of power users, is at hand to purchase the surplus gas (or waste heat), it might with great advantage be utilised in an adjacent chemical factory. For there is no reason why the crude tars, benzols, and naphthalene produced on the coking plant should not be refined and transformed into other more valuable products in a chemical factory on the spot, the heat and power for which would be wholly derived from the surplus gases. Or, alternatively, any chemical operations requiring cheap electric current might very well be carried out in factories erected in close proximity to by-product coking plants.

As a Raw Material in the Chemical Industry.—Coke-oven gas is an important source of the hydrogen used in the synthetic ammonia industry. Thus Pollitt[1] stated that 15·8% of the total amount of hydrogen used throughout the world for ammonia synthesis in 1930–31 was derived from coke-oven gas. According to Pallemaerts,[2] the relative costs of preparing hydrogen at a pioneer installation for the manufacture of synthetic ammonia at Ostend, were:

(i) From water-gas (from coke at 19·6*d.* per ton) 8·7*d.* per 1,000 cu. ft., and (ii) from coke-oven gas (at 5·45*d.* per 1,000 cu. ft.) 9·27*d.* per 1,000 cu. ft.

The residual gas, after removal of hydrogen, has a calorific value some 25% higher than that of the coke-oven gas, and could be delivered into the mains for industrial purposes. On the other hand, during the preparation of hydrogen from the gas, three fractions are obtained, (i) a fraction containing about 18% of carbon monoxide and 73% of nitrogen, which is used on the Continent for the synthesis of methanol, (ii) a fraction containing about 75% of methane, and having a calorific value of about 815 B.Th.U. per cu. ft., which would be suitable as a raw material for synthetic reactions, and (iii) a fraction containing approximately equal parts of ethylene, ethane, and methane, together with a little propylene and carbon monoxide, which is used at Béthune for production of ethyl and propyl alcohols.

Literature.—W. A. Bone and G. W. Himus, " Coal, Its Constitution and Uses," Chap. XXII, 1936; and J. Roberts and A. Jenkner, " International Coal Carbonisation," 1934.

W. A. B. and G. W. H.

BENZOL RECOVERY BY ACTIVE CHARCOAL.

This process for the recovery of benzol from coal gas is described in detail on account of its importance in connection with motor fuel production. In this country some 33 million tons of coal are carbonised annually by the gas and coke-oven industries, and in 1934 the annual total production of refined benzol from all sources had reached just over 32 million gallons. This production could be more than doubled if all the coal gas made were submitted to treatment. In the carbonisation of 1 ton of coal about 3 gallons of benzol are formed. Part of the benzol is found in the tar, but the bulk of it accompanies the gas in which it is present at a partial pressure of 7 to 8 mm. Formerly the recovery of this benzol was impracticable, but the adoption of by-product coke-ovens and the substitution of heating for illuminating standards in the gas industry have rendered possible the practice of extraction processes on a large scale. Prior to 1929 the only commercial method in this country was that of absorption by heavy oil, which is still most widely used. The active charcoal process was originated by the Bayer Company (G.P. 310092, 1916 ; B.P. 156543, 1916 ; A. Engelhardt, Gas-u. Wasserfach, 1921, **64**, 205 ; 1922, **65**, 473) and is fairly well known on the Continent. A disability of the process as first introduced was the short working life of the adsorbent, but this difficulty has now been largely overcome (H. Hollings, S. Pexton and R. Chaplin, Trans. Inst. Chem. Eng. 1929, **7**, 102 ; Gas J. 1929, **188**, 715). In 1929 the first commercial unit was installed by the Gas, Light & Coke Company at Harrow, and a few years later a large plant was erected at Beckton (H. Hollings and S. Hay, J.S.C.I. 1934, **53**, 143). The active charcoal process has certain technical advantages over the oil process, and is likely to be more widely adopted in the future.

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[1] World Power Conference, Berlin (1930).

[2] Second International Conference on Bituminous Coal, Pittsburgh (1928).

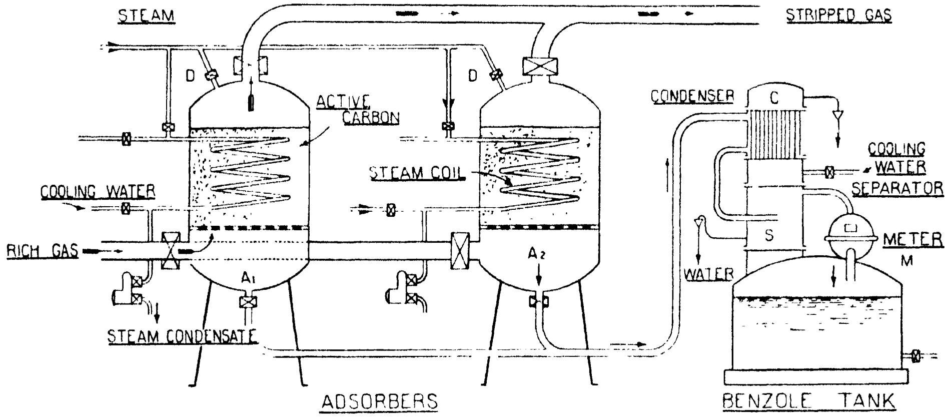

FIG. 1. [*Reproduced by the courtesy of the J.S.C.I.*

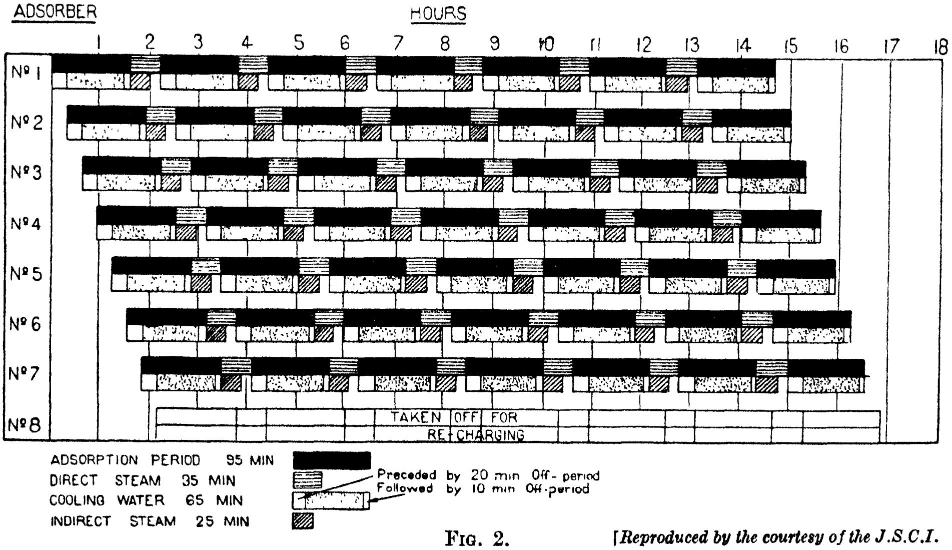

FIG. 2. [*Reproduced by the courtesy of the J.S.C.I.*

Description of the Process.—Chemically activated charcoal of high volume activity and low retentivity is used in the form of short rods or pellets 4 to 5 mm. in diameter. The gas to be treated must be free from tar fog, hydrogen sulphide and naphthalene, and the charcoal plant is accordingly placed at a point in the stream where the gas is in this state. The process is shown diagrammatically in Fig. 1. Gas passes upward through adsorber A1,

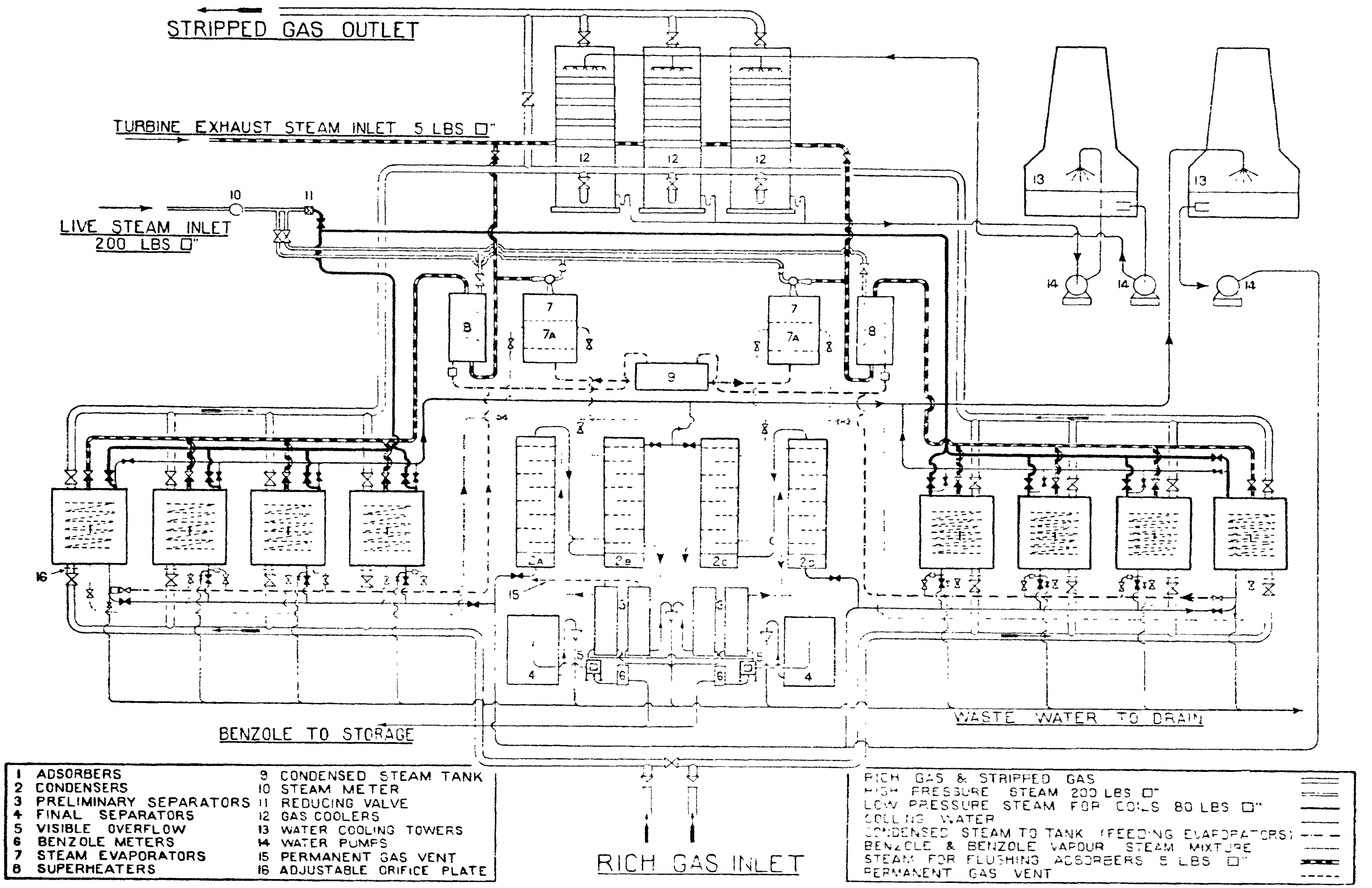

FIG. 3.

[*Reproduced by the courtesy of the J.S.C.I.*

containing active charcoal, which retains benzol and certain other constituents of the gas (*e.g.* unsaturated hydrocarbons and carbon disulphide), cold water being circulated through the coils at the same time. When the charcoal in A1 is saturated the gas is diverted to adsorber A2, while A1 is regenerated. For this purpose the cooling water is shut off and steam is passed through the coils in order to heat the charcoal. At the same time direct steam is passed downwards through the charcoal bed to remove the adsorbed benzol. The mixture of steam and benzol vapour leaving the adsorber passes to the condenser C, and the condensed liquids are separated in the gravity separator S, from which the benzol flows through the meter M to storage tanks, while the water runs to waste. When steaming is completed gas is again admitted to the hot adsorber which removes excess moisture and cools the charcoal rapidly. After a short time cooling water is again circulated through the coils and adsorption carried to completion. The cycle of operations is thus repeated. The size and number of adsorbers required are determined by the volume of gas to be treated in unit time, but not less than two adsorbers can be used if the adsorption process is to be continuous (*see* time schedule, Fig. 2 on p. 271).

THE BECKTON PLANT.—This installation deals with gas from horizontal retorts and coke ovens and has a potential output of 20,000 gallons of benzol per day, recovering 2·9 gallons from 10,000 cu. ft. of gas with an efficiency of 92–95%. The layout of the plant is shown in Fig. 3. It is arranged in two halves which can be operated as a single unit or independently. Each half has its individual gas inlet main and contains four adsorbers. The adsorbers (Fig. 4) are cylindrical vessels, 9 ft. in diameter and 27 ft. in length, and hold 7 tons (700 cu. ft.) of active charcoal, which is supported on hinged grids. The charcoal is packed about pipe coils used for heating and cooling. The charcoal is charged into the adsorbers from closed containers which are run into position on overhead trucks. For discharging the charcoal the grids are lowered at the centre by means of special gear and the spent material received into similar containers placed underneath. Communication between the two levels is effected by a hydraulic lift. Overhead cranes are provided for assembling and dismantling parts of the plant. Each half of the plant is provided with a steam regenerator, a set of tubular condensers, a set of preliminary separators, a final separator, and a benzol meter. The stripped gas is cooled by direct contact with water in three gas coolers which condense the water removed from the hot charcoal after steaming. Cooling water for all purposes is supplied by electric pumps, but the water circulated through the adsorber coils is contained in a closed system charged with de-aerated, condensed steam to minimise corrosion.

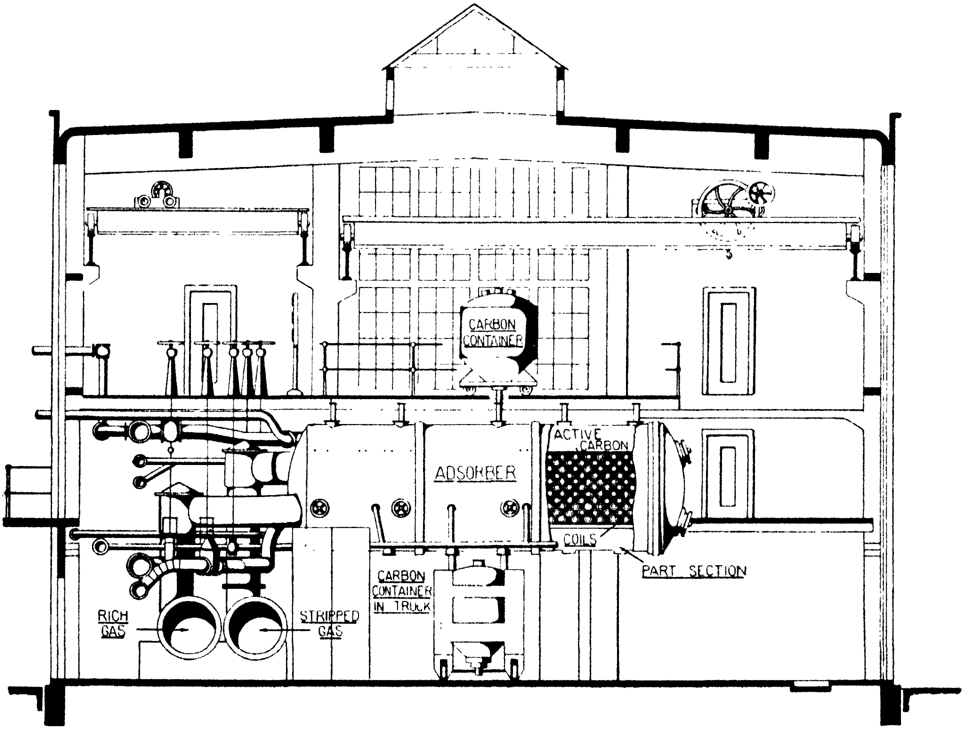

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FIG. 4.

Operation of Plant.—There is considerable latitude in the rate of passing gas which may vary from 300,000 to one million cu. ft. per hour per adsorber. The number of adsorbers at work is governed by the amount of gas being made and by the age, *i.e.* activity, of the charcoal in use. At full capacity five are under gas, two under steam, and the remaining one either in reserve or being recharged. Gas is passed until the benzol "breakpoint" is reached as indicated by flat flame burners fed from the outlet stream. The stripped gas at first burns with a practically non-luminous flame, but as little as 0·04 gallon of benzol per 10,000 cu. ft. of filtered gas shows as a luminous fringe in the flame. In steaming, the direct and indirect steam supplies are turned on simultaneously. The adsorbed *gases* first evolved contain benzol and are returned to the inlet stream. After 5 or 6 minutes, at a temperature of 80°C., benzol commences to be evolved. Steaming is continued 30 to 40 minutes, according to the age of the charcoal, which is finally raised to a temperature of 125°C., and contains 15% moisture. In the subsequent adsorption cycle cooling water is not used for the first 20 minutes, so that the charcoal may be sufficiently dried by the rich gas.

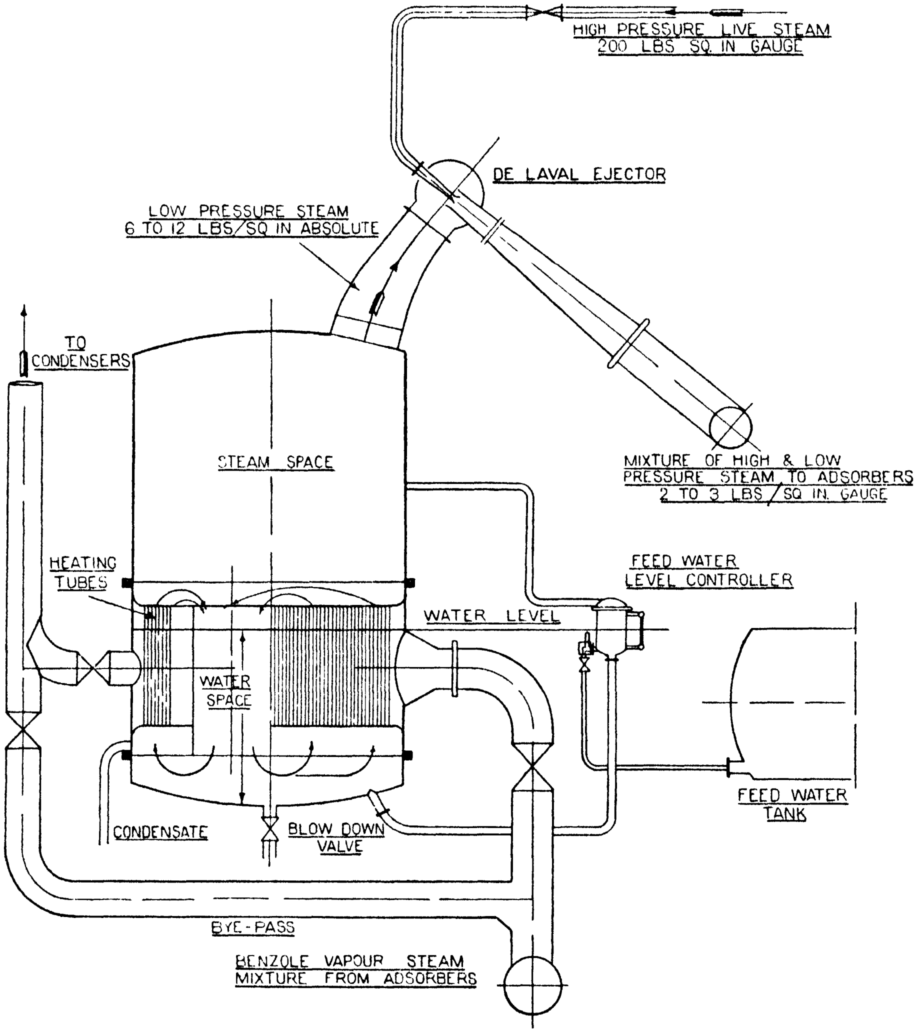
HIGH PRESSURE LIVE STEAM 200 LBS SQ. IN GAUGE
DE LAVAL EJECTOR
LOW PRESSURE STEAM 6 TO 12 LBS/SQ IN ABSOLUTE
TO CONDENSERS
STEAM SPACE
MIXTURE OF HIGH & LOW PRESSURE STEAM TO ADSORBERS 2 TO 3 LBS/SQ IN. GAUGE
HEATING TUBES
FEED WATER LEVEL CONTROLLER
WATER LEVEL
WATER SPACE
FEED WATER TANK
CONDENSATE
BLOW DOWN VALVE
BYE-PASS
BENZOLE VAPOUR STEAM MIXTURE FROM ADSORBERS

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Fig. 5.

Steam Requirements.—Direct steam is used at 2 to 3 lb. pressure and is made up partly of steam from high pressure mains and partly of steam produced in the steam regenerator (Fig. 5). Cheap exhaust steam may replace a considerable part of the high pressure steam when two adsorbers are steamed simultaneously, as the table shows. Indirect or coil steam is taken from high pressure mains after reduction to 80 lb. pressure, and de-superheating. Requirements and distribution of process steam are shown in the following table.

	Steaming one adsorber.	Steaming two adsorbers at once.
	lb.	lb.
Indirect, to coils . .	1,000	2,000
Direct steam :		
(*a*) High pressure steam	6,000	6,000
(*b*) Regenerator steam	4,500	5,000
(*c*) Exhaust steam .	—	10,000
	11,500	23,000

About 6% only of the total heat requirements of the process are accounted for by the latent and sensible heats of the benzol. The rest is used in raising the temperature of the adsorber and contents. The average overall steam consumption is about 34 lb. per gallon of benzol.

The Steam Regenerators.—These are an important feature of the plant and supply 32% of the heat contained in the distillate leaving the adsorbers. A regenerator is shown diagrammatically in Fig. 5. Distillation vapours from the adsorbers pass between a nest of tubes between two header plates before entering the condensers. A De Laval steam ejector in communication with the top of the chamber produces a partial vacuum and lowers the boiling-point of the water in the tubes so that heat is transferred from the vapours to the steam produced which is entrained by the high pressure steam in the ejector. The feed water consists of condensate from the adsorber coils augmented by softened water from outside sources and is maintained at constant level by a float valve. The two regenerators supply between them 4,500 lb. of steam per cycle.

Practical Aspects of the Process.—The adsorptive capacity of the charcoal varies but slightly with changes in benzol concentration in the gas, *e.g.* an increase from 2·13 to 2·85 gallons per 10,000 cu. ft. only increases the capacity from 32 to 33% by weight of adsorbent. Since the "slip" of benzol is unaltered the recovery efficiency is also increased. The adsorptive capacity is considerably lowered by the presence of moisture in the charcoal or in the gas. It is therefore an advantage to have the gas as dry as possible.

The efficiency of recovery of benzol increases by about 1·2% per degree C. fall in temperature; hence one reason for cooling the charcoal during adsorption. The heat of adsorption of benzol (340 B.Th.U. per lb.) is sufficient to raise the charcoal temperature to 140°C., but this is dissipated at such a rate by the coil water, effluent gas, etc., that the adsorption temperature remains in the region of 20°C. The most effective cooling is provided by evaporation of residual moisture in the adsorbent which lowers the temperature from 120°C. to 60°C. in 20 minutes, and is of great importance in prolonging the working life of the adsorbent.

The last traces of benzol are difficult to remove from the charcoal and practically desorption is at an end when the ratio of direct steam to recovered benzol is 10 : 1, *i.e.* after about 20 minutes. At this point, however, the charcoal temperature is too low for efficient drying, so that steaming is continued for a further 10 to 20 minutes (the newer, *i.e.* the more active, the adsorbent, the greater is the amount of steam required).

Depreciation of the Adsorbent.—Hydrocarbons of high molecular weight and certain unsaturated hydrocarbons adsorbed from the gas are preferentially retained by the charcoal after steaming. These accumulate in the charcoal and gradually impair its activity towards benzol. The unsaturated hydrocarbons are particularly troublesome in this respect because when the charcoal is heated they polymerise into gummy substances for which the adsorbent has a high capacity, and which can only be removed by oxidation at high temperatures. The rapid deterioration of the adsorbent proved to be a serious disability of the active charcoal process which was at first uneconomic through this cause (H. Hollings, S. Pexton and R. Chaplin, *l.c.*). Operative procedure has now been so much improved that the adsorbent can be used from 1,500 to 1,900 times, and made to recover about 175 times its own weight of benzol before needing replacement. The following practices are mainly responsible for this improvement:

(i) the passage of steam countercurrent to gas;
(ii) the simultaneous use of direct and indirect steam at high rate, which limits the heating period;
(iii) the adjustment of a critical moisture content in the charcoal after steaming so that it cools rapidly in contact with rich gas.

In this connection the employment of charcoal of low retentivity, *i.e.* of low capacity under the desorption conditions of the process, is obviously important.

Spent charcoal contains about 33% of fouling material, but may contain as much as 45%. A more or less complete regeneration may be brought about by the action of air or of steam with air at 500–600°C. (B.P. 313154 and 338500, 1929). In these processes the fouling matter is carbonised and burnt away but a certain loss of adsorbent is inevitable. A recent process based on hydrogenation of the fouling material under pressure, and which entails no loss of adsorbent, is described under B.P. 374597, 1932.

Sulphur Removal.—In adsorbing benzol active charcoal also removes sulphur compounds from the gas. Practically all the carbon disulphide and thiophen are removed in the early stages, but as the benzol breakpoint is approached some carbon disulphide and other volatile sulphur compounds are displaced into the filtered gas. Fig. 6 shows in a typical manner the variation of total sulphur content of the outlet gas from a 1-ton adsorber up to the benzol breakpoint. At this point the *average* sulphur content of the filtered gas corresponds with a purification efficiency of 75–80%, which compares favourably with processes specifically devised for sulphur removal. Higher purification efficiencies could be obtained by reducing the ratio of gas to charcoal, but such reduction would lower the benzol output of the plant and increase the consumption of steam per unit of benzol recovered.

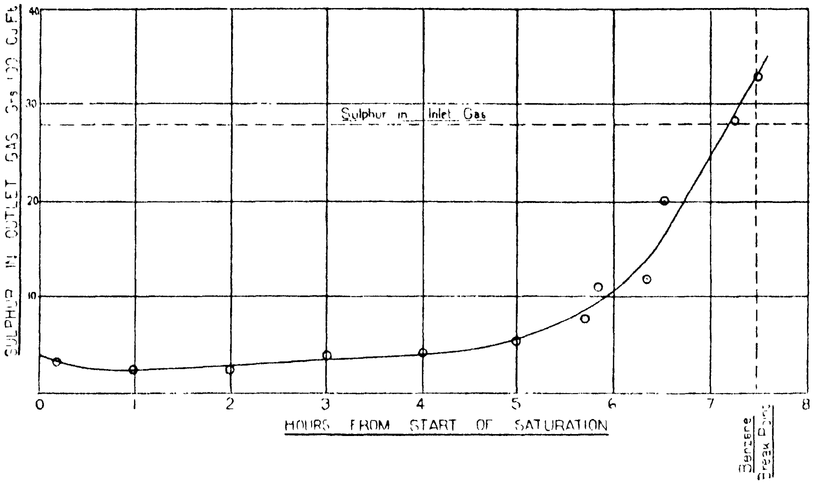

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FIG. 6.

Points in favour of the active charcoal process are:

(i) high recovery efficiency;
(ii) low steam, water, and power consumption;
(iii) purification of the gas from sulphur.

From the economic point of view there seems little to choose between the active charcoal and oil processes (*v.* Adsorption, Vol. I. p. 150*a*).

R. C.

COLAMINE *v.* CHOLINE.

COLCHICEÏNE *v.* COLCHICUM.

COLCHICINE *v.* COLCHICUM.

COLCHICINIC ACID *v.* COLCHICUM.

COLCHICUM and COLCHICINE. *Colchicum autumnale* Linn. (Fam. Liliaceæ), Meadow saffron (Fr. *Colchique*, Ger. *Herbstzeitlose*); the plant is found in meadows and pastures throughout Europe, where its crocus-like flowers, usually of a lilac hue, occur in September and October.

The Brussels conference agreed that the seeds only should be used; in the "British Pharmacopœia," 1932, the seeds and corms are official; in the "United States Pharmacopœia," 1936, the seeds and the alkaloid colchicine are official. The alkaloidal content of the plant varies greatly, mostly from 0·2 to 0·8% in the seeds ("British Pharmacopœia"; 1932, not less than 0·3%; "United States Pharmacopœia," 1936, not less than 0·45%), from 0·1 to 0·5 in the corms ("British Pharmacopœia," 1932, not less than 0·25%). Colchicine occurs to a slight extent also in the flowers.

Colchicine is present in other species of the same genus and also in the large tubers of *Gloriosa superba* (Fam. Liliaceæ) common in India and Ceylon (0·3% of "gloriosine," Clewer, Green and Tutin, J.C.S. 1915, **107**, 839). Klein and Pollauf (A. 1931, 778) found colchicine in considerable quantities in the following Liliaceæ: *Bulbocodium*, *Tofieldia*, *Veratrum anthericum*, *Hemerocallis*, *Ornithogalum*, *Tulipa*; *cf.* also Albo (J.C.S. 1901, **80**, II, 679). Fourment and Roques (Amer. Chem. Abstr. 1927, **21**, 2166) isolated colchicine from *Merendera Bulbocodium* (Fam. Liliaceæ).

Extraction of Colchicine.—The alkaloid occurs as free base in the plants; all preparations of colchicine are based on its removal from acid or neutral solution by $CHCl_3$. Chemnitius (J. pr. Chem. 1928, [ii], **118**, 29) proceeds as follows: Ground seeds are exhausted with hot 80% EtOH and the solvent evaporated. Fat and resins are removed by addition of molten paraffin-wax to the still warm concentrated solution, which when solidified can be removed mechanically. Water is added to precipitate further amounts of tarry material. From the aqueous solution the base is then shaken into $CHCl_3$, this solvent evaporated and last traces removed by distillation with absolute EtOH. The chloroform-free alcoholic solution is filtered and the alkaloid precipitated with four times its volume of Et_2O, when a slightly yellow semi-crystalline powder melting between 135° and 145° is obtained. The salicylate is then usually prepared.

For accurate assay of the seeds, *see* "British Pharmacopœia," 1932, p. 131; and "United States Pharmacopœia," 1936, p. 127. Further references, *see* Self and Corfield (B. 1932, 1135), Hooper and King (Pharm. J. 1923, **111**, 104), Grier (*ibid.* 87).

For microchemical identification of colchicine with platinirhodanide, *see* Klein and Pollauf (*l.c.* 1931), colour reactions of colchicine, *see* Ekkert (A. 1926, 533 ; *ibid.* 1929, 86), estimation of colchicine with phosphotungstic acid, *see* Davies (Amer. Chem. Abstr. 1921, **15**, 3894).

Colchicine (I), $C_{22}H_{25}O_6N$, $[\alpha]_D^{16\cdot5}$ −120·6° (in $CHCl_3$) and −429° (in H_2O), m.p. 155–157°, soft pale yellow needles from $CH_3{\cdot}CO_2Et$ (Clewer, Green and Tutin, *l.c.* 1915). The alkaloid is usually seen as a yellow anhydrous varnish, m.p. 142°–147° ; Zeisel first crystallised it from $CHCl_3$ with two molecules of $CHCl_3$ of crystallisation ; according to Merck (Pharm. Zentr. 1916, **57**, 619) there are two such compounds, $B{\cdot}CHCl_3$ and $B_2{\cdot}CHCl_3$. The crystalline colchicine is mostly the latter compound in which 14–16% $CHCl_3$ is retained tenaciously, and is only given off slowly at 100°. According to Merck, pure (I), dissolved in 3 parts of H_2O, slowly crystallises as the hydrate $B_2{\cdot}3H_2O$.

(I) dissolves slowly but abundantly in H_2O, readily in dilute $EtOH$, $CHCl_3$, and hot benzene, less readily in hot H_2O (12%) or absolute $EtOH$, hardly at all in Et_2O.

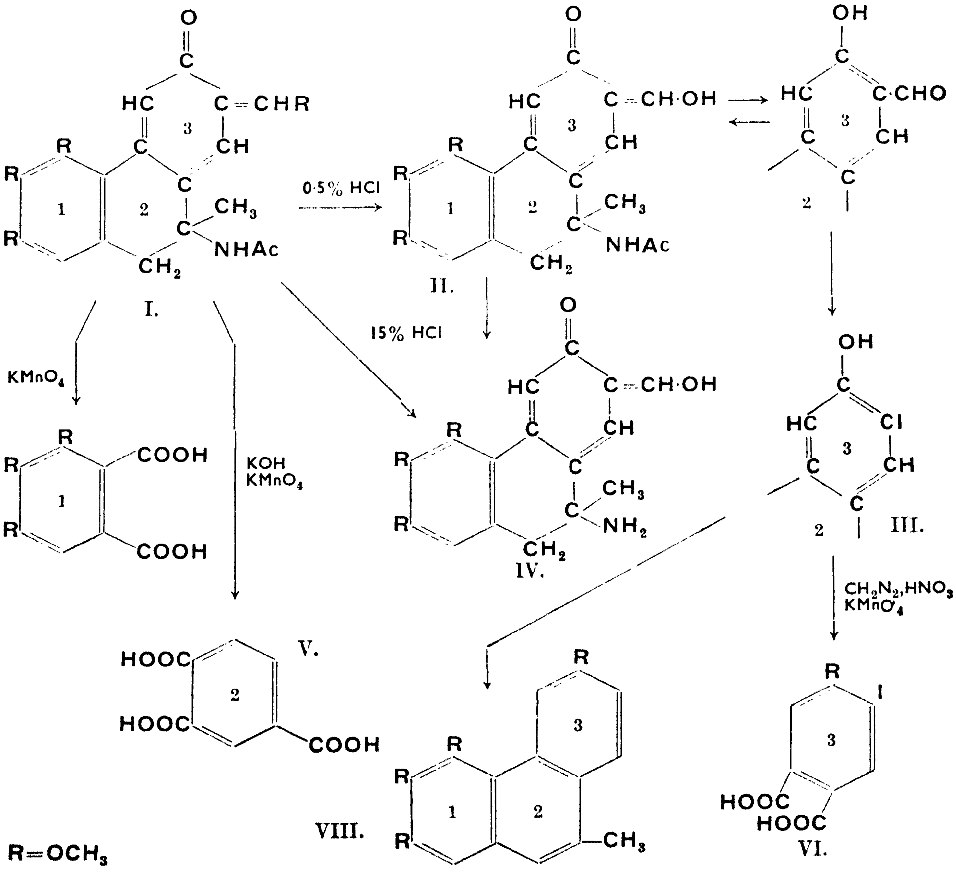
Being an acid amide, (I) is a very feeble base and one of the few alkaloids which can be extracted from acid solution by $CHCl_3$. No salts are formed except an aurichloride, m.p. 209°. Dilute mineral acids and alkalis colour colchicine solutions intense yellow. HNO_3 (*d* 1·4) colours the solid alkaloid a deep violet, changing to yellow and finally to green (characteristic). Tannic acid, phosphomolybdic acid, potassium triiodide, and bismuth potassium iodide are the most sensitive precipitants. For dissociation of (I), *see* Kolthoff (Biochem. Z. 1925, **162**, 348) ; for absorption-spectrum of (I), *see* Purvis (J.C.S. 1927, 2715).

Constitution of Colchicine.—Early work on the constitution of (I) is due to Zeisel and co-workers (Monatsh. 1883, **4**, 162 ; 1886, **7**, 557 ; 1888, **9**, 865 ; 1913, **34**, 1327, 1339), but only the brilliant research of Windaus and co-workers gave definite information (J.C.S. 1911, **100**, I, 904 ; 1915, **108**, I, 708 ; 1924, **126**, I, 72 ; Annalen, 1924, **439**, 59 ; Ber. 1924, **57**, [B], 1871, 1875).

(I) contains a *N*-acetyl and four MeO-groups ; if it is heated for a short time with 0·5%HCl or weak alkali, *colchiceïne* (II) is formed with loss of one MeO-group. Contrary to (I), which is a practically neutral substance, (II),

$$C_{21}H_{23}O_6N,\tfrac{1}{2}H_2O,$$

has weakly acidic properties ; m.p. 139°, or anhydrous m.p. 172° ; it gives a green



coloration with ferric chloride characteristic for an enolic form of a β-keto-aldehyde (keto-hydroxy-methylene grouping, tautomeric with an *o*-hydroxy-aldehyde).

By methylation (II) is transformed back to colchicine and *N*-methyl-colchicine. By the action of hypoiodite the enolic aldehyde group in (II) is replaced by iodine, a transformation characteristic of *o*- and *p*-hydroxy-aldehydes, the resulting compound is called *N-acetyl-iodocolchinol*, $C_{20}H_{22}O_5NI$ (III).

If (I) is heated with 15% HCl the *N*-acetyl-group is removed as well as one MeO-group and *trimethylcolchicinic acid*, $C_{19}H_{21}O_5N$ (IV), results. The latter compound yields salts with alkalis and acids. By treating (IV) with hydroiodic acid, the remaining three MeO-groups are removed and *colchicinic* acid results.

By oxidation of (I), (II), (III), or (IV) with permanganate 3:4:5-trimethoxyphthalic (from ring 1) and succinic acids are obtained. By potash fusion and subsequent permanganate oxidation terephthalic and *trimellitic* (V) (1:2:4-benzenetricarboxylic) acids are obtained, indicating the presence of a second six-membered ring (ring 2).

N-acetyl-iodocolchinol (*see above*) has a phenolic OH-group and can easily be methylated. If this methyl ether is oxidised first with nitric acid and then with permanganate, rings 1 and 2 are destroyed and *iodo-methoxy-phthalic acid* (VI) is isolated from the oxidation mixture. This latter acid originates from the third six-membered ring present in (I).

The methylether of (III) (*see above*) can be reduced (elimination of iodine) and hydrolysed (elimination of acetyl-group) to colchinol-methylether, $C_{19}H_{23}O_4N$; this compound is then submitted to a Hofmann degradation, which eliminates NH_3 and generates a double bond in the central ring, forming 2:3:4:6-tetramethoxy-9-methylphenanthrene (VIII). This compound was further transformed into 9-methylphenanthrene, which was identical with a synthetic product.

(I) is the only known alkaloid which does not contain a heterocyclic *N*-atom yet is highly poisonous. This may be connected with the fact that *Colchicum autumnale* belongs to the monocotyledons usually devoid of any alkaloidal constituents.

For tetrahydrocolchicine, *see* D.R.P. 279999, for octahydrocolchicine, $C_{22}H_{33}O_6N$, *see* Windaus (Annalen, 1924, **439**, 74). (II) does not occur naturally; if obtained by extraction of colchicum, it is a secondary degradation product.

Physiological Action of Colchicum.—Colchicum is employed in medicine chiefly as a remedy in gout and rheumatism, and colchicine itself, mostly as the salicylate, has been similarly used. The alkaloid is highly poisonous and not more than 3–4 mg of crystalline (I) per diem should be given ; lethal dose for rabbits 4 mg., for mice 3 mg., for dogs and cats 1 mg. per kg. of bodyweight. (I) is a slow poison which only acts after an incubation period, very similar to the one of bacterial toxins. Owing to its slow absorption (possibly by the gradual formation of an oxidation derivative) into the central nervous system, no symptoms are shown for several hours after its administration. It first excites and then paralyses the nerve endings. (I) causes acute intestinal pain with nausea and diarrhœa, and in mammals poisoned with (I) the alimentary canal shows all the symptoms of acute gastro-enteritis.

Cf. Winterstein, " Die Alkaloide," Berlin, 1927, p. 147 ; and Henry, "Plant Alkaloids," 2nd ed., p. 391.

Schl.

COLCOTHAR (syn. Caput mortuum). The reddish-brown residue of ferric oxide formerly obtained in the manufacture of fuming oil of vitriol from iron sulphate.

COLEMANITE. A hydrated calcium borate, $Ca_2B_6O_{11},5H_2O$, containing 50·9% boron trioxide. It is found in California at Death Valley in Inyo Co., and in the Calico district in San Bernardino Co. ; and although not discovered until 1882 and 1883, is now of some importance as a material for the preparation of borax and boracic acid. Cavities in the massive, white material are lined with beautiful, water-clear crystals with a profusion of brilliant facets ; these are monoclinic, with a perfect, pearly cleavage parallel to the plane of symmetry. They are considerably harder (H. 4–4½) than borax ; sp.gr. 2·42. The mineral forms, together with other borates and borosilicates, a bed 7 to 10 ft. in thickness in sandstones and clays.

The compact minerals, *priceite* from Oregon and *pandermite* from Asia Minor, have very nearly the same composition

$$(Ca_5B_{12}O_{23},9H_2O),$$

and they have been regarded as impure, massive varieties of colemanite. E. S. Larsen (1917) has, however, by an examination of the optical characters established the identity of priceite and pandermite, and proved them to be triclinic and distinct from colemanite. These also are mined as borates.

L. J. S.

COLLARGOL. Colloidal compound of albumen and silver, containing 70% or more Ag.

COLLIDINES. Trimethylpyridines are so-called, *e.g.* 1:3:5 and 1:3:4.

COLLIN. A preparation made by heating an extract of hide powder or solution gelatin with caustic soda and neutralising with acetic acid. Used in the analysis of tannin and tanning materials (Parker and Payne, J.S.C.I. 1904, **23**, 648 ; Wood and Trotman, *ibid.* 1071).

COLLIRON. Colloidal iron, 10%, with a trace of copper, used for treatment of anæmias (*Evans Sons, Lescher, and Webb, Liverpool*). B.P.C.

COLLODION (syn. Collodium) *v.* CELLULOID PLASTICS.

COLLODION COTTON *v.* CELLULOSE LACQUERS.

COLLOIDS. As by far the greater part of matter, both organic and inorganic, with which man is normally familiar is in the colloid state, there is hardly a branch of science or technology where colloid concepts have not been applied, and hence the literature of the subject is both voluminous and diverse. The development of colloid science still continues to be very rapid, and several journals are devoted to it alone, while papers on colloid science appear in all the general journals of pure and applied chemistry.

Colloidal sols of gold, ferric hydroxide, etc., were known by the middle of the last century, and Faraday with characteristic perspicacity attributed the properties of a gold sol prepared by him to the metal being in an exceedingly fine state of subdivision. In 1861 Graham showed that substances which are normally easy to crystallise are characterised by a high rate of diffusion and by the power to pass through certain animal or vegetable membranes ; such substances, which included the common electrolytes as well as sugars, etc., he termed ***crystalloids***. A further class of materials, including starch, soaps, many dyes, gums, proteins, etc., which are difficult to obtain in a crystalline form, were found to be characterised by a low rate of diffusion and inability to pass through membranes ; these substances were termed *colloids*. This separation of colloids from crystalloids by dialysis, a process depending on the inability of the former to pass through parchment or collodion membranes, is still widely used.

The term colloid is now employed in quite a different sense from that in which Graham used it, and it is to be considered as referring not to a special class of chemical compounds (although proteins, many dyes, etc., normally form colloids spontaneously) but to a state in which all compounds and elements are capable of existing. From our present standpoint colloids are treated as special examples of two-component systems in which one substance (the disperse phase) is distributed uniformly in the other (dispersion medium or continuous phase). Such dispersed systems can be classified into three types according to the fineness of division or degree of dispersion of the disperse phase : (*a*) mechanical suspensions, (*b*) colloidal solutions, (*c*) molecular solutions.

The smallest particles which are visible under the microscope are of the order of about 0·1 μ, while the average molecular size is about 0·1 mμ. Between these limits lies the region of colloidal particles, a substance thus being strictly defined as being in the colloidal state if its particles of size 1–100 mμ are distributed in a continuous medium. It should be realised that there is no clearly defined line of demarcation between the three groups of disperse systems, the colloids being differentiated for practical purposes by their physical properties form a continuously graded series.

The colloidal state is characterised by the predominating influence of surface. The enormous increase in surface area on subdivision of a cube of unit dimensions is given in the table at the top of next column (Wo. Ostwald).

Length of side of cubes in cms.	No. of cubes	Total area.	
1	1	6 cm.^{2}	
10^{-1}	10^3	60 cm.^{2}	
10^{-2}	10^6	600 cm.^{2}	region of coarse suspensions, emulsions, etc.
10^{-3}	10^9	6,000 cm.^{2}	
$10^{-4} = 1\ \mu$	10^{12}	6 m.^{2}	upper limit of Brownian movement.
$10^{-5} = 0{\cdot}1\ \mu$	10^{15}	60 m.^{2}	colloidal dimensions.
$10^{-6} = 0{\cdot}01\ \mu$	10^{18}	600 m.^{2}	
$10^{-7} = 0{\cdot}001\ \mu = 1\ \text{m}\mu$.	10^{21}	6,000 m.^{2}	
$10^{-8} = 0{\cdot}1\ \text{m}\mu = 1\text{A}$	10^{24}	60,000 m.^{2}	molecular dimensions.

As subdivision increases to molecular dimensions, intermolecular and interionic forces become of primary importance, so that the effect of surface and hence of adsorption is greatest in the middle of the colloidal range, in the so-called "zone of maximum colloidality." The term colloid should be extended to include all substances (such as charcoal, silica gel, pyrophoric metals) whose surface properties predominate over those due to chemical constitution.

The complete list of possible two-component disperse systems is given below, the dispersion medium being placed first, followed by the disperse phase :

(1) Solid+solid (ruby glass, alloys).
(2) Solid+liquid (solid emulsions, minerals with sealed liquids).
(3) Solid+gas (solid foams, porous solids).
(4) Liquid+solid (suspensions).
(5) Liquid+liquid (emulsions).
(6) Liquid+gas (foams and froths).
(7) Gas+solid (smoke, cosmic dust).
(8) Gas+liquid (mist, clouds).

Although it is possible to obtain all the above in colloidal dimensions, Nos. 4 and 5 have received by far the greater portion of study and will alone be considered here. Colloidal suspensions whether of solid particles or liquid droplets are termed *sols*.

Classification of Colloids.—Colloidal sols differ widely in properties but fall into two broad classes, of which colloidal gold and gelatine respectively are prototypes. The chief differences which serve to classify the two groups of colloids are as follows :

Gold sol type.	Gelatine sol type.
Artificial inorganic colloids.	Natural complex substances.
Viscosity almost the same as that of water.	High viscosity.
Concentration always low.	High concentration possible.
Sensitive to small concentration of electrolytes.	"Salted out" only by high electrolyte concentration.
Do not swell, unsolvated.	Highly solvated, considerable swelling.
Coagulate to form coarse granules, irreversible.	Coagulate to jelly, generally reversible.

It must be realised that the ideal examples of the two types are extreme cases of the diversity of colloid properties and that there exist numerous colloids (*e.g.* the hydrous oxides and hydroxides) whose properties are intermediate. The most prevalent usage at the moment terms the two classes of colloids *hydrophobic* and *hydrophilic* according to whether they "hate" or "love" the dispersion medium—water—or *lyophobic* and *lyophilic* when the classification is generalised to include all kinds of dispersion media. Gold forms a hydrophobic sol since it does not disperse spontaneously and is easily separated (*e.g.* by electrolytes) from the dispersion medium. Gelatine, on the other hand, is hydrophilic as it disperses spontaneously, is stable and, at the same time, becomes highly hydrated. Another type of classification terms the first class of colloids *suspensoid*, the dispersed particles being solid, and the second class *emulsoid*, it being assumed, chiefly by analogy with coarser emulsions and from viscosity considerations, that gelatine and other similar substances exist in the form of liquid droplets when dispersed in water. There is much to be said for this theory, but it should be pointed out that mercury and certain other emulsoid sols (*e.g.* dilute oil emulsions) are of the gold type, and that in any case the distinction between solid and liquid tends to disappear in the colloidal range where surface tension effects become all-important. The chief distinction between the two main classes of colloids is almost certainly due to solvation.

COLLOIDS AND THE ULTRAMICROSCOPE.—The heterogeneity of colloidal sols is clearly shown by the Tyndall effect, for though the sol may appear to be perfectly clear by transmitted light, when a strong beam of light is concentrated in the sol, its path is marked by an opalescence and the resulting light is polarised. This effect is caused by the scattering of light by the dispersed particles of the sol. It should be pointed out here that solutions of crystalloids (*e.g.* sugar) also give a faint Tyndall cone, especially when examined by ultra-violet light, and that even the purest water is not completely optically void. When the Tyndall cone is brought to a focus within the sol and the small volume, thus brilliantly illuminated, examined through a microscope from above, the light scattered vertically by the sol particles is observed in the microscope. This is the principle of the original slit ultramicroscope of Zsigmondy and Siedentopf (Ann. Physique, 1903, [iv], **10**, 1), the optical arrangements of which are shown below.

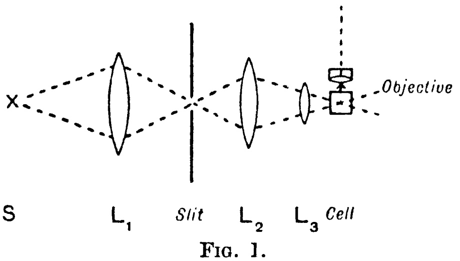


FIG. 1.

Since no direct light enters the microscope, the scattering particles appear as a number of bright spots of light against a dark background; it is, of course, not possible to see the actual colloid particles by the ultramicroscope, but only the halo of light scattered by each particle. The lower limit of the ultramicroscope is 5–10 mμ, so that highly dispersed sols of definitely colloidal characteristics appear homogeneous when examined by this means. The intensity of the scattered light depends on the difference of refractive index between the two phases of the disperse system, and so highly solvated colloids such as gelatine in water are difficult to examine by this method. Despite these limitations the ultramicroscope has proved to be one of the most powerful weapons of the colloid chemist. Many optical modifications of the ultramicroscope have been introduced.

The most striking feature of the ultramicroscope image is the rapid and unceasing motion of the particles—a phenomenon similar to the *Brownian movement* exhibited by small particles such as pollen grains, gamboge, oil droplets, etc., in water, which is visible in the ordinary microscope (R. Brown, Phil. Mag. 1828, **4**, 161; 1829, **6**, 161; Edin. New Phil. Journ. 1828, **5**, 358; 1830, **8**, 41). It was soon realised that this movement was due to the impact of molecules on the colloidal particles, impacts on all sides not cancelling instantaneously, and that a visual representation of molecular motion in liquids as pictured by the kinetic theory was thus obtained. The frequency of motion increases with degree of dispersion. It has been deduced theoretically by Einstein and Smoluchowski and demonstrated experimentally by Svedberg that colloid particles possess the same kinetic energy as gas or dissolved molecules, and are subject to the same laws (*see* osmotic pressure, below). From the Brownian movement, calculations of the rate of movement of molecular particles have been made which are in good agreement with the value as deduced from the kinetic theory; the value of the Avogadro constant N has also been calculated by Perrin, who obtained the value $N = 6\cdot5 \times 10^{23}$ for gum mastic particles of radius 6·5 μ.

THE PREPARATION OF COLLOIDS.—As the colloidal state is intermediate between mechanical suspensions and molecular solutions, colloidal sols may be prepared either by dispersion of the former or condensation of the latter. Of *dispersion methods* the simplest is the *spontaneous disperion* of natural colloids, such as gelatine or soap in water, cotton in cuprammonium hydroxide and the formation of *organosols* of nitro- or acetyl-cellulose, rubber, resins, etc. in organic liquids. *Mechanical dispersion* has received a good deal of industrial attention especially since the advent of the colloid mill. In one of the commonest types of mill the substance to be dispersed, mixed with the dispersion medium, is made to pass between two metal discs, placed close to one another and rotating at very high speeds in opposite directions (or between a stator and a rotor). In this process the coarse suspension particles are torn so as to yield particles approaching colloid dimensions. It is generally necessary to have a *dispersing agent* present in the initial mixture, otherwise the fine suspension coagulates spontaneously. Owing to the high cost of running and maintenance, colloid mills are not an unqualified commercial success. For a detailed account of colloid mills, *see* P. M. Travis, "Mechano-chemistry," New York, 1928, where the practical applications of fine suspensions are discussed. Liquid-liquid systems can be easily dispersed mechanically, but, except where very dilute emulsions are required, an *emulsifying agent* has to be added. *Electrodispersion* was first introduced by Bredig (Z. Elektrochem. 1898, **4**, 514) who prepared metallic sols by arcing wires of the metal beneath the surface of the dispersion medium. Svedberg has modified this method by enclosing the wires in a silica tube which has a hole bored in front of the arc. The metal vapour produced in the arc is blown out by a stream of inert gas and condenses to a sol in the dispersion medium, which is thus not subjected to the decomposing influence of the arc. The high frequency oscillatory arc has also been used with great success to produce highly dispersed sols of practically all the metals and by a modification of the method ether sols of the alkali metals were prepared. Dispersions of solids in gases can be produced *explosively* by condensing the gas under pressure in the pores of a solid and then releasing the pressure (*see* Sata, Bull. Chem. Soc. Japan, 1936, **11**, 443). Volcanic dust is produced in this way. One of the most important dispersion methods is that of *peptisation*, in which a coarse suspension is dispersed to a sol by the action of an electrolyte ; simple examples are the peptisation of arsenic sulphide by hydrogen sulphide and of ferric hydroxide by a small quantity of ferric chloride.

Condensation methods of dispersion are more numerous. Amongst the simpler methods may be mentioned *solubility reduction* on cooling (*e.g.* sulphur in alcohol) and the effect of *solvent change* (*e.g.* by dropping an alcoholic solution of gum mastic into water), while the formation of organosols may be accomplished by the *simultaneous condensation* of a metal vapour with that of its organic dispersion medium (Roginski and Schalnikov, Kolloid-Z. 1927, **43**, 67) the applications of this method are limited by the fact that the metal must be capable of subliming at a temperature at which the liquid does not char. Another interesting method makes use of the silent electric discharge (Miyamoto, J. Chem. Soc. Japan, 1934, **55**, 1273) whereby colloidal arsenic can be prepared from arsine and hydrogen. By far the most important condensation method of colloid formation is that of carefully controlled *chemical reaction*. It has been established by von Weimarn that precipitation from either very dilute or very concentrated solution yields a colloidal product, whereas at medium concentrations normal precipitates are obtained ; excellent examples are afforded by the precipitation of barium sulphate and of Prussian blue. The formation of colloidal materials at high concentrations is at first sight unexpected, but the explanation is presumably that, formed in such close proximity, the molecules have no time to arrange themselves into a regular crystalline lattice, but remain in an amorphous condition. This is borne out by the fact that these amorphous, high concentration sols are unstable and age with the formation of normal crystalline aggregates. Nearly every type of reaction in solution can thus be made to produce colloidal sols, amongst the most useful may be mentioned the following : reduction (preparation of metallic sols by hydrogen, carbon monoxide, and numerous organic reducing agents), oxidation (*e.g.* oxidation of hydrogen sulphide to give a sulphur sol), hydrolysis (formation of $Fe(OH)_3$ sol by hydrolysis of $FeCl_3$; silica gel), double decomposition (formation of sols of acids, bases, and salts), polymerisation (vinyl esters, styrene, etc., Staudinger, Ber. 1926, **59** [B] 3019). To show the wide range of possible reactions, mention may be made of the formation of colloidal sodium chloride by double decomposition of thionyl chloride and sodium salicylate and the production of colloidal palladium hydride by the adsorption of hydrogen by a palladium sol (prepared by reduction) ; the hydride sol is an excellent catalytic reducing agent. For practical details of colloid preparation, *see* Svedberg, "Formation of Colloids" (1921) ; Holmes, "Laboratory Manual of Colloid Chemistry" (1927) ; Reitstötter, "Die Herstellung kolloider Lösungen anorganischer Stoffe" (1927).

The Purification of Colloids.—Dialysis, the classical method of separating sols from electrolytes is still widely used, dialysers of parchment or collodion, which are constructed so as to have as large a surface as possible, being the most efficient. As this process, depending entirely on diffusion, is somewhat slow, the method of electrodialysis has been introduced, in which the electrolyte ions are made to migrate away from the sol on the passage of an electric current. The apparatus for electrodialysis is shown schematically below :

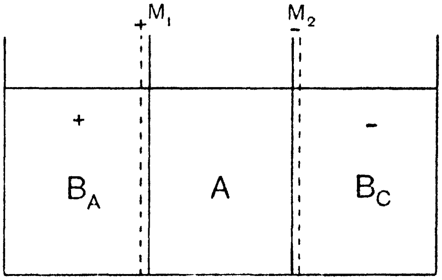


Fig. 2.

The sol is enclosed in the compartment A, separated from B_A and B_C by the dialysis membranes M_1 and M_2, close to which the electrodes (dotted lines) are placed. The anode should be of platinum, the cathode may be of copper or any other suitable metal. There are three effects contributing to the separation of ions from the colloid : (*a*) as in the case of ordinary dialysis, diffusion, (*b*) migration of ions through the membranes to the electrodes, (*c*) electro-osmotic streaming of the liquid. In order that the third cause should be effective, the anode membrane should be positively charged (prepared from albuminoid materials) and the cathode membrane negatively charged (collodion or parchment).

Substances in colloidal suspension pass readily through filter papers, but, if the close relationship between colloids and mechanical suspensions is borne in mind, it will be realised that if the pore size is sufficiently reduced, it ought to be possible to retain colloids by filtration, while allowing water as well as dissolved ions and molecules to pass through. This has been successfully carried out by using gelatinous materials, the pores of which are of colloidal dimensions and can be varied in size by modifications in the methods of preparation. The greatest degree of success has been attained by *ultrafilters* of collodion supported in the pores of filter paper. As the concentration of the impregnating material is increased, the permeability of the filter decreases, so that a series of graded filters can be prepared which may be employed not only to purify colloids, but to sort out the particles according to their sizes (Bechhold, Z. physikal. Chem. 1907, **60**, 257). The pore size of ultrafilters may be calculated from the volume of water forced through unit filter area in unit time by a given pressure. It may be stated that ultrafiltration depends not only on the sieve action of the ultrapores but also on the charge on the filter. Collodion filters are negatively charged in presence of water and allow the passage of negative particles more readily than of positive ones. This renders determination of absolute size by ultrafiltration somewhat doubtful. Electro-ultrafiltration is a device to speed up ultrafiltration in the same way that electro-dialysis quickens dialysis. The relative rates of separation of electrolytes and non-electrolytes by the four methods are given in the following table (E. Heymann, Z. physikal. Chem. 1925, **118**, 65), a potential gradient of 40 v./cm. being used in the electrical processes :

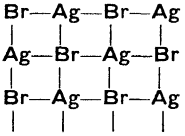
Process.	NaCl	Cane sugar.
Dialysis	1	0·3
Electrodialysis	168	2 (?)
Ultrafiltration	14	14
Electro-ultrafiltration . .	182	14

(For a review of the literature on ultrafiltration and an account of the separation of single proteins, rubber latex, acetone collodion, etc., by this means, *see* Ferry, Chem. Rev., June, 1936.)

ADSORPTION.—The enormous surface of contact between disperse phase and dispersion medium possessed by substances dispersed colloidally has already been stressed. This is chiefly important because of the ions or molecules which can be attached at the interface by adsorption and thus modify the stability and properties of the system. The term adsorption is here used to indicate a concentration or attachment of some substances at the interface. In a two-phase system where one of the phases is a liquid it follows on thermodynamical grounds from surface tension considerations that the most stable relation between the two phases is the one characterised by a minimum surface tension. Hence, if there is present in the liquid a substance which lowers its surface tension, this substance will accumulate in the surface layer. The relationship as strictly deduced by Gibbs is $U = -\frac{C}{RT}\frac{d\sigma}{dC}$, where U is the excess of substance at the interface, C its concentration in the bulk of the liquid, σ the surface tension, R the gas constant, and T the absolute temperature. It is seen that when increasing concentration reduces the surface tension, U becomes positive ; when it increases the surface tension U is negative, indicating a concentration in the bulk of the liquid away from the surface. This negative adsorption should obviously be of a much lesser magnitude than normal adsorption, which is in accord with the experimental facts. On the other hand, a relatively minute quantity of a surface or capillary active compound will reduce the surface tension enormously The fatty acids which are particularly effective in reducing the surface tension show an increasing activity with increasing number of carbon atoms in the homologous series (Traube's rule). It is interesting to note also that adsorption of these substances on charcoal increases in the same order. Capillary active substances (*e.g.* the soaps) also act often as emulsifying agents in liquid-liquid dispersion ; this property is closely connected with the fact that there is a definite molecular orientation in the adsorbed surface layer.

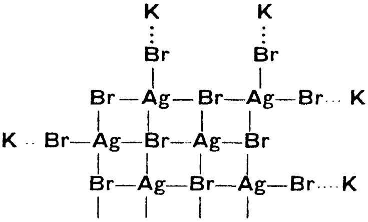
Gibb's isotherm cannot be applied directly to solid surfaces where $d\sigma/dC$ cannot be measured. The solid surface is always very complicated even with apparently plane crystalline surfaces of metals or salts, there are numerous deep fissures (Smeckal cracks) between the blocks of crystals, as well as peaks and valleys on the surface. Atoms on peaks or edges are less strongly attached to the body of the material and are consequently very active for adsorption and catalysis. Much evidence on active centres has recently been obtained by the study of differential catalyst poisoning which conclusively demonstrates the existence of different types of surface atoms. Active centres, which are often capable of fixing ions or molecular groups chemically, are of fundamental importance in colloidal behaviour. For solid surfaces, the empirical sorption isotherm of Freundlich, $\frac{x}{m} = kC^{\frac{1}{n}}$ (where x is the amount adsorbed, m the weight of adsorbent, C the equilibrium concentration, and k and n constants), is generally applicable (*see*, however, J. W. McBain, "The Sorption of Gases and Vapours by Solids," London, 1932. p. 5).

When an adsorbing surface is placed in contact with an electrolyte solution it can generally be shown that the electrolyte is not adsorbed as a whole, but that one ion is more strongly adsorbed than the other. If, for example, a colloid adsorbs the anion preferentially, the excess of cations will arrange themselves as an outer ionic atmosphere, the complete formation of adsorbed and outer ions constituting an electrical double layer. The colloid surface and nature of the double layer is well illustrated by the precipitation of the silver halides. In the space lattice of silver bromide, of which a two dimensional representation is given on Fig. 3*a*, each interior silver or bromide ion is surrounded by six equidistant ions of the opposite sign. The silver ions on the *surface*, however, are only surrounded by five equidistant bromide ions (three in the plane of the paper, one in front and one behind), and similarly each surface bromide ion is surrounded by only five silver ions ; each surface ion thus lacks one ion of the opposite sign to saturate its affinity. When the particle is present in a solution of potassium bromide, bromide ions are preferentially adsorbed from solution on to surface silver ions ; as the added bromide ions are already balanced by corresponding potassium ions, a second but more mobile adsorbed layer (of potassium ions) is formed all over the surface, with the result that an electrical double layer is formed and the particle becomes a stable negative colloid (*see* Fig. 3*b*).



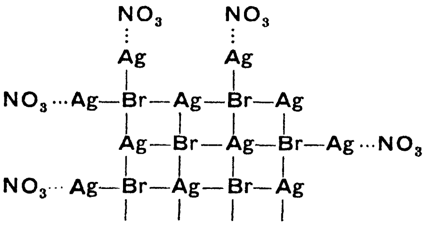
Neutral particle.

FIG. 3*a*.



Negative sol particle (in KBr).

FIG. 3*b*.



Positive sol particle (in $AgNO_3$).

FIG. 3*c*.

At the point where equivalent amounts of potassium bromide and silver nitrate are present the particles are coagulated as a normal uncharged precipitate, but if an excess of silver nitrate is present a positive sol results, according to the scheme in Fig. 3*c*. It will be observed that the facts outlined above give an explanation based on adsorption of the phenomenon of peptisation already mentioned; it is seldom, however, that peptisation adsorption is quite as simple as the case cited here. Further reference to this type of adsorption will be found in the following sections.

ELECTRICAL PROPERTIES OF COLLOIDS.—It has already been mentioned that the particles of a colloidal sol are electrically charged, a property which they share with suspensions and other surfaces. A qualitative determination of the sign of the charge of a colloid may be made by a simple adsorption experiment, positive colloids being adsorbed by negative adsorbents such as silica gel, and negative colloids by positive adsorbents such as aluminium hydroxide. The sign of the charge, however, is not usually dependent on the physical nature of the compound which forms the sol but, as will be evident from the case of silver bromide already discussed, is influenced by such quantities of electrolytes as may be adsorbed from the solution.

If a direct current is passed through a colloidal sol, the charged particles move towards one or other of the electrodes ; this movement is known as *cataphoresis* and can be measured by the moving boundary method, the boundary being seen by means of a Tyndall cone ; if the colloid is colourless ultra-violet light may be used. The Hittorf transport method can also be applied to cataphoresis, but by far the most satisfactory and convenient measurements are made by observing the movement of the actual particles across the field of the ultramicroscope. When the moving particles are discharged at the electrodes, they coagulate, an observation which suggests a close relationship between electrical charge and stability, a matter which will be discussed in the next section. The effect of small quantities of electrolyte on the cataphoretic velocity is particularly marked, the influence of the ion of charge opposite to that of the colloid increasing very greatly with valency. If, instead of allowing the particles to move in the electric field, they are held stationary in the form of a diaphragm, the potential difference between disperse phase and dispersion medium manifests itself by a movement of the dispersion medium towards one or other of the electrodes, the direction being the opposite of that in which the diaphragm would move if free. This effect, which is known as *electrical endosmose* or *electro-osmosis*, is influenced by the presence of electrolytes, etc., in the same way as cataphoresis. Two other related electrokinetic phenomena have been investigated, namely the *streaming potential* developed by forcing a liquid through a diaphragm, and the converse *sedimentation potential* produced by the passage of solid particles through a liquid under gravity. The electrokinetic potential (ζ) is related to the cataphoretic velocity (u) by the following equation :

$$u=\frac{Dx\zeta,}{4\pi\eta}$$

where D is the dielectric constant of the medium, η its viscosity, and x the potential gradient. The velocity of migration of colloidal particles is of the same order as that of ions.

The origin of the electric charge on colloidal particles has been much discussed, one school maintaining that it is due to the adsorption of ions from solution, the other that the charges are produced from the ionogenic substance which forms the disperse phase (*see below*). It is now almost certain that both causes operate simultaneously in most cases, one or the other predominating with different types of colloid. It is clear also that the charge on the colloid particle is compensated by an equal and opposite (ionic) charge in the liquid in immediate contact with it, the system as a whole being (like an electrolyte solution) uncharged. The whole system of colloid particle plus compensating double layer (*gegenions*) is often termed a *micelle*. On passing an electric current, the two parts of the double layer tend to move in opposite directions, thus setting up an opposing e.m.f. The *intermicellar* liquid which is a conductor tends to compensate this, so that there is a net movement of the micelle towards the electrode. With organosols, where the liquid is a non-conductor, the disturbances must be electronic rather than ionic, but it should be pointed out that the presence of a very small trace of water plays an important part here.

The classical theory of Helmholz assumed the double layer to be compact, there being an abrupt potential gradient between the two phases. This concept has been modified by the diffuse double layer theory mainly due to Gouy (J. Phys. Radium 1910, **9**, 457), and it is now considered that although the inner layer is probably rigid, the gegenion layer is diffuse and extends outwards a distance of a few mμ. The proportion of positive gegenions (in a negative sol) decreases and that of negative ions in the outer layer increases with increasing distance from the interface. The presence of electrolyte in the intermicellar liquid influences the diffuse layer, the thickness of which decreases with increasing concentration of electrolyte.

Some confusion existed as to the relationship between the Nernst electrochemical potential (ϵ) and the electrokinetic potential (ζ), but Freundlich has succeeded in measuring both potentials for the system glass-water, and it is now realised that they do not necessarily bear any relationship to one another. The electrochemical potential represents the total potential drop between the disperse phase and the body of the dispersion medium and is little affected by the presence of ions in the latter. The electrokinetic potential, on the other hand, is the potential between the interior, rigid portion of the double layer and the body of the liquid, and is thus only a constituent part of the electrochemical potential ; it will be smaller than the latter, but its magnitude and sign depend on the ions which are present. The electrokinetic potential thus represents the potential across the plane of shear.

The actual chemical nature of the double layer must now be discussed in more detail. It was early assumed that a neutral substance when placed in water would become negatively charged owing to a preferential adsorption of the hydroxyl ion ; a basic substance such as ferric oxide would in the same way adsorb the hydrogen ion preferentially and so become positively charged, the compensating hydroxyl ions forming the diffuse layer. With electrolyte solutions a particle will become charged by preferential adsorption of one of the ions in the manner which has already been illustrated by silver bromide.

The concept of ionogenic substances forming the double layer develops directly from a study of soap solutions. The sodium salts of the lower fatty acids behave as normal binary electrolytes, but in the case of the higher members it becomes obvious that association is taking place and that colloidal character is being assumed. The anion is no longer a discrete fatty acid anion in solution, but an aggregate of fatty acid ions together with undissociated salt molecules ; the colloidal aggregate is really a giant polyvalent ion dissociated at the surface and compensated by an equivalent number of sodium ions in solution in close proximity to the giant ion. When an electric current is passed, the outer sodium ions move to the cathode, the giant ions to the anode. Since the latter contain a large number of undissociated soap molecules in the interior, it follows that some of the sodium migrates to the anode. This and other work by McBain on soap micelles indicates that, in the case of such definite colloidal electrolytes at least, cataphoresis is a special instance of electrolysis. Similar considerations apply to sols of most dyes and to many other organic colloids. An attempt has been made, chiefly by Pauli and his co-workers, to extend the idea of colloidal electrolytes to ordinary sols. In the case of a positive hydroxide sol prepared by hydrolysis of ferric chloride, the micelle is represented as :

$$\left|\begin{array}{c} a\mathrm{Fe_2O_3} \\ b\mathrm{FeOCl}\quad c\mathrm{H_2O} \end{array}\right| \!-\! x\overset{+}{\mathrm{FeO}} + x\overset{-}{\mathrm{Cl}}$$

The positive charge is contributed by certain active centres of FeO on the surface, the negative charge of the diffuse layer consisting of an equivalent number of Cl ions. Part of the Cl is enclosed within the sol particle (as FeOCl) and thus has little influence on the properties of the sol. Such colloidal ions may carry several thousand unit charges ; the number of chemical molecules (excluding those of the water) per unit charge is termed the *colloid equivalent*. The classical and modern theories of electrochemistry are being applied with some success to colloids, regarded as complex electrolytes. McBain and Thomas (J. Physical Chem. 1936, **40**, 997) have shown that the transport numbers of ferric oxide sols as well as of the true colloid electrolytes (soaps, etc.) can be measured by means of the normal (*e.g.* Hittorf analytical and moving boundary) methods. But it is difficult to see how the ionogenic theory can be extended to covalent organic substances in which the formation of ionic double layers is improbable but which still display electrokinetic properties.

Electrokinetic measurements on proteins, viruses, bacteria spermatazoa, etc., are yielding valuable results. For a full account of this type of work as well as for the theory of electrokinetic phenomena, *see* Abrahamson, " Electrokinetic Phenomena " (1934). *See also* the Faraday Society discussion on colloidal electrolytes (Trans. Faraday Soc. 1935, **31**, 1) and a useful chapter on the electrical properties of colloidal systems by E. Heymann in Bechhold's " Einfuhrung in die Lehre von den Kolloiden."

Colloid Stability.—The essential characteristics of a particle in colloid suspension are its fine state of division, with which is associated the Brownian movement, and the electric charge which it carries. On subdivision of a solid, as surface area increases, so does surface energy, and thus, according to thermodynamic principles, colloid particles should have a tendency to aggregation. The rate at which a particle of given size should settle in a liquid under the influence of gravity is given by Stoke's law :

$$V=\frac{2r^2(d_1-d_2)g}{9\eta},$$

where d_1 and d_2 are the densities of disperse phase and dispersion medium respectively, V the velocity of the particle of radius r in liquid of viscosity η. The application of Stoke's law to particles of colloid dimensions shows, for example, that a gold particle of size 10 $\mathrm{m}\mu$ should fall through 1 cm. of water in 29 days, while a benzene sphere of the same size would take about 12 years. Convection and other disturbing influences would normally mask this small rate of settling, so that colloidal solutions in the absence of special influences which encourage coagulation are indefinitely stable. The Brownian movement is manifested as a small diffusion effect superimposed on the external forces of gravity, etc. The Brownian movement, bringing about as it does collisions of the suspended particles, favours aggregation when the impinging particles are uncharged. It is the electric charges on the particles which, by producing mutual repulsion, condition the stability of the sol ; uncharged particles of colloidal dimensions, unless protected, coagulate immediately. It has been shown in the case of dilute oil suspensions, that a slow coagulation takes place even when the globules are still feebly charged, indicating that under these conditions only a proportion of the total number of collisions results in coalescence. Coagulation is purely an aggregation effect which is followed by precipitation due to gravity according to Stoke's law ; the initially amorphous precipitate may then gradually become crystalline.

COAGULATION OF HYDROPHOBIC SOLS.—The effect of electrolytes on the cataphoretic velocity of normal hydrophobic sols has already been mentioned. These systems are influenced by minute amounts of ions, the particles moving more and more slowly as the electrolyte concentration increases until, when the velocity is zero, the sol coagulates, only to be peptised and the particles made to move in the opposite direction if electrolyte addition is continued.

When the colloidal particle is uncharged and does not move in the electric field it is said to be at the *isoelectric point*, which condition is usually marked by a p_H value characteristic of the system. The effect of electrolytes and consequent coagulation of a colloid is an adsorption effect which is due to the antagonistic influence of the separate ions ; ions having the same sign as those conditioning the charge of the colloidal particle, tend to increase the electrokinetic potential, those of opposite sign to decrease it or change the sign. The ions which bring about coagulation are thus those of opposite sign to that of the colloid, and in an electrolyte solution it is those ions which generally have the predominating influence. Although H^+ and OH^- ions are particularly potent in this connection, the effectiveness of the ion in inducing coagulation increases rapidly with valency, metal ions of the same valency all exerting approximately the same effect. The flocculation values (in millimols. per litre), representing the minimum concentration of various electrolytes necessary to coagulate a negative arsenic sulphide sol, have been shown by Freundlich to be :

$NaCl=51$
$KCl=50$
$KNO_3=50$
$MgSO_4=0{\cdot}81$
$CaCl_2=0{\cdot}65$
$SrCl_2=0{\cdot}63$
$ZnCl_2=0{\cdot}68$
$AlCl_3=0{\cdot}093$
$Ce(NO_3)_3=0{\cdot}080$

The anion has obviously little influence in the coagulation of the negative sol and the flocculation value varies very considerably with the cation valency. When a positive ferric hydroxide sol is investigated, the cation has little effect and the anion valency becomes the predominating factor. Some minimum flocculation concentrations in this case are :

$KNO_2=12$
$KCl=9$
$\frac{1}{2}BaCl_2=9{\cdot}6$
$K_2SO_4=0{\cdot}26$
$MgSO_4=0{\cdot}22$
$K_2Cr_2O_7=0{\cdot}14$

Freundlich (Z. physikal. Chem. 1910, **73**, 385) has explained these facts by assuming ions of the same valency to be adsorbed by the colloid to an approximately equal extent. Equal concentrations of any ion of a given valency will thus be required to reduce the electrokinetic potential to zero, and consequently the flocculation value will be the same for all such ions. These concentrations being small, they will appear in the initial part of the adsorption isotherm where the amount adsorbed increases very rapidly with concentration. Supposing that the *amount* of a univalent ion which has to be adsorbed in order to bring about coagulation is double that of a divalent ion and three times that of a trivalent ion, the steep rise in the adsorption isotherm makes it clear that the actual *concentration* of salts required to produce this effect is not in the simple ratio $1:\frac{1}{2}:\frac{1}{3}$, but in the ratio indicated by the experimental results, trivalent ions having a disproportionately large effect. Many ions, especially of the heavy metals and of organic complexes, can be shown by analysis to be more strongly adsorbed than those of the simple ions discussed here, and thus have lower flocculation values than those tabulated above. According to the "chemical" theory of colloidal electrolytes, coagulation is to be regarded as a type of double decomposition ; when a ferric hydroxide sol with chlorine as gegenion is coagulated by sodium sulphate, for example, sodium and chlorine ions remain in solution while the sulphate ion is attached to the precipitate.

Although the adsorption theory of coagulation proposed by Freundlich has proved to be a useful working hypothesis, it fails to explain many aspects of the coagulation of hydrophobic colloids. For a complete understanding of this problem the influence of the coagulating ions on the sol double layer has to be studied. The modern point of view is clearly given by Verwey in "Hydrophobic Colloids," a report of a symposium held in Utrecht, 1937 (Centen, Amsterdam).

When two colloidal sols of the same charge are mixed, there is little notable effect, but when the charges are of different sign coagulation may take place if there is roughly the same amount of each present, otherwise the one which is in excess in part remains dissolved.

The stability of colloidal sols generally decreases with temperature increase, a smaller concentration of electrolyte being necessary to induce coagulation at higher temperatures. Although this effect may often be due to solution of electrolytes from the walls of the containing vessel, results of Reid and Burton (J. Physical Chem. 1928, **32**, 425) show that in some cases heat alone may bring about coagulation. Amongst other coagulating influences may be mentioned mechanical agitation and the effect of radiation of various sorts (ultra-violet light, X-radiations, radioactive rays). The latter effects may often be explained by a photochemical action on protective colloids, peptising electrolytes, etc. Bacterial suspensions may be coagulated by electrolytes in the same way as ordinary sols.

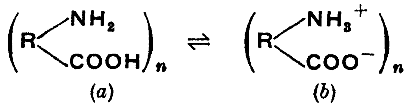
It is interesting to note that concentrated solutions of electrolytes, and especially of strong acids, differ so much from dilute solutions that colloids, far from being coagulated, are maintained in stable suspension in them. Voet (J. Physical Chem. 1936, **40**, 307) has prepared sols of inorganic compounds in strong sulphuric and phosphoric acids and in certain concentrated salt solutions.

From what has already been said, it is obvious that peptisation is due to adsorption effects of a similar nature to those which cause coagulation of already peptised systems, namely preferential adsorption of positive or of negative ions. Sata (Kolloid-Z. 1935, **73**, 50) claims to have peptised ferric hydroxide by means of ultrasonic waves, even in the absence of electrolytes.

STABILITY OF HYDROPHILIC COLLOIDS.—Hydrophilic colloids are on the whole much more stable than are hydrophobic colloids, although the stability is more dependent on chemical constitution; small amounts of protein decomposition products produced by hydrolysis on heating may influence the properties of the sol considerably. Hydrophilic colloids at once differentiate themselves from hydrophobic sols by their greater inertness towards electrolytes. The former type is indeed precipitated by a large concentration of electrolyte, but the amount is so much greater that the term "salting out" is used to distinguish the effect from ordinary hydrophobic coagulation. Hydrophilic particles are charged in the normal way, the charges being capable of progressive neutralisation by adsorption of ions to an iso-electric point. Hydrophilic colloids do not, however, coagulate at the iso-electric point, although this is their point of minimum stability. This increased stability as compared with hydrophobic colloids is due to hydration, the sol particles being covered by a water layer like truly dissolved substances. Coagulation in this instance can thus be brought about by simultaneous discharge of the stablising charge and removal of the stabilising water sheath. An important series of observations on this subject was made by Kruyt (Kolloid-Beih. 1926, **28**, 1), who showed that a negatively charged agar sol became discharged on the addition of small quantities of electrolyte but was still stable owing to its water sheath. If a dehydrating substance such as alcohol or acetone were now added, the colloid coagulated. On the other hand, if a similar amount of dehydrating agent were added before the addition of electrolyte, the water sheath was destroyed but the sol remained stable owing to its negative charge. Such a dehydrated hydrophilic sol behaved exactly like a normal hydrophobic colloid, being flocculated by small amounts of electrolyte, the concentration and valency effects of which were exactly the same as with a negative arsenic sulphide sol.

In view of what has just been said it becomes clear that the "salting out" effect of electrolytes on hydrophilic colloids is due to their dehydrating action as well as to their power of neutralising the charge. As the former effect demands a much larger concentration of electrolyte than the latter, it is apparent that the minimum concentration required to bring about coagulation will depend essentially on the dehydrating power of the salts; there is thus little noticeable valency effect, in contrast to that of hydrophobic coagulation. When a number of sodium salts are arranged in order of "salting out" efficiency, the following sequence is obtained: citrate > tartrate > sulphate > acetate > chloride > nitrate > chlorate > iodide > thiocyanate. This is the so-called Hofmeister or lyotropic series and is the same as that which represents the power of these electrolytes in "salting out" organic compounds from their solutions and of reducing the solubility of gases in water; in the Hofmeister series, therefore, the salts are arranged in order of their hydration. In practice sulphates of sodium or magnesium are used for the salting out of colloids because of their high solubility as well as position in the series. Salts at the end of the Hofmeister series such as iodides and thiocyanates are not capable even in saturated solution of coagulating hydrophilic colloids; on the contrary, they have a high dispersive power, being able to "dissolve" cellulose and other normally insoluble substances.

The proteins are the most important of the naturally occurring hydrophilic colloids; the behaviour of these substances the electrokinetic properties of which are greatly influenced by H^+ and OH^- and little by other ions, is best interpreted by considering them to be amphoteric electrolytes similar to but much more complicated than the amino acids.



(a) (b)

As the proteins contain both acid and basic groups, they form salts both with bases and acids. In alkaline solution (*e.g.* **NaOH**) the acid groups are active and a sodium salt is formed which dissociates to some extent to produce sodium ions and a negative anion. In alkaline solution, therefore, proteins are generally negatively charged and wander to the anode. In the presence of excess acid (*e.g.* **HCl**) the basic groups form chloride derivatives which dissociate to form protein cations and chloride gegenions ; the protein is positively charged in these circumstances and wanders to the cathode. There must obviously be some hydrogen ion concentration at which the particles are uncharged or at any rate acidic and basic to an equal extent ; this *isoelectric point* depends on the relative strength of the acid and basic groups and is thus not necessarily at $p_H = 7$. The isoelectric point is readily determined by cataphoresis, for here the mobility is zero ; it can also be measured by precipitation, viscosity, potentiometric titration, etc. There is evidence that at the isoelectric point proteins exist as "zwitterions" (formula *b*) rather than as neutral molecules (*a*). The isoelectric point is a specific property of each individual protein and is usually well on the acid side of neutrality, but the isoelectric point of hæmoglobin is at $p_H = 7$. Proteins behave normally in having their minimum stability at the isoelectric point.

SENSITISATION AND PROTECTION.—When minute amounts of a hydrophilic colloid such as gelatine are added to a hydrophobic sol, the stability and cataphoretic velocity of the latter are reduced although actual coagulation may not occur. This effect is probably due to the normal adsorption of the sensitising particles which behave as colloidal electrolytes ; the charge on the hydrophobic sol is thus reduced and unstability results. It is found that sensitisation only occurs when the protein film is incomplete, and the ingenious idea has been put forward that it may thus be due to simultaneous adsorption of the hydrophilic colloid particle by two or more hydrophobic particles which are thus brought into close contact. When sufficient gelatine (or other hydrophilic colloid) is present to form a complete coating on the hydrophobic particles, the latter take on a typical hydrophilic character and are inert to small concentrations of electrolytes ; such a system is termed a protected sol.

A gold sol or an oil emulsion may be flocculated by 0·003% gelatine, although larger, and much larger amounts stabilise.

The protection of sols is of great importance and has been practised empirically since ancient times. Zsigmondy showed that the sharp colour change from red to blue displayed by gold sols under the influence of electrolytes could be used as a means of obtaining a quantitative comparison of the protective action of different colloids. The colour change supposed to be due to aggregation is inhibited by protection. He defined the *gold number* of a protective colloid as the number of milligrams which are just sufficient to prevent such a colour change on the addition of 1 c.c. of 10% sodium chloride solution to 10 c.c. of a standard gold sol. The greater the efficiency of the protector, therefore, the smaller the gold number. An alternative method of measurement is by the ***rubin number*** of Wo. Ostwald, in which the weight of colloid in 100 c.c. of solution which will just prevent change of colour in a Congo-rubin sol similar to that of the gold sol is the criterion. The gold and rubin numbers of a few protective colloids are shown in the table :

Colloid.	Gold number.	Rubin number.
Gelatine and glue .	0·005–0·01	0·025
Isinglass . . .	0·01–0·02	—
Sodium caseinate .	0·01	0·004
Hæmoglobin . .	0·03–0·07	0·008
Albumin . . .	0·1–0·2	0·020
Sodium oleate . .	0·4–1·0	—
Dextrin . . .	6–20	—
Potato starch . .	*c.* 25	*c.* 0·2
Silica sol . . .	∞	∞

In many biological systems double or multiple protection is effective ; thus in milk, which is essentially an emulsion of fat droplets in water, some workers consider the oil-water interface to be protected by casein which in turn is protected by the more efficient lactalbumin. The proportion of lactalbumin to casein in cow's, human and ass's milk is 0·175, 1·2, and 3·31 respectively. Of the three varieties, cow's milk is much the most readily coagulated by acids and by rennin, the function of the latter seems to be to convert lactalbumin by enzyme action to a coagulant. In agreement with the figures quoted the coagulum of cow's milk is much coarser than that of the others. Cow's milk is thus much less digestible for an infant than is human or ass's milk but may be protected by the addition of gelatine, dextrin, Irish moss, and other protectors and even by sodium citrate or tartrate, which also possess general protective action.

Protection is essentially an adsorption phenomenon ; this is demonstrated by the fact that a finite time interval must elapse after the addition of gelatine to a hydrophobic sol, before protection is complete ; further, although the degree of protection is determined by the concentration of protective colloid used, once a hydrophobic sol is protected, dilution does not diminish this effect. It is generally most convenient to assume that the particles of the protected sol are covered by a complete layer of protector or that, at any rate, its active centres are thus shielded, but Zsigmondy has demonstrated ultramicroscopically that, when the particles of hydrophobic sol are small compared with those of the protector, one particle of the latter may adsorb several of the former with the usual protective effects. There is, however, no relationship between the sign of the charge of the hydrophobic colloid and protective action, proteins, for example, being capable of protecting both positive and negative sols. The protected sol assumes the electrical properties of its protector ; a quartz suspension protected by gelatine will possess the cataphoretic velocity and isoelectric point of gelatine.

Protective colloids have considerable industrial importance and there is an extensive patent literature. As an example may be mentioned the dispersion of colloidal graphite in water (*Aquadag*) or oil (*Oildag*) in the presence of the protective tannic acid; such preparations have valuable lubricating properties. This process, invented by Acheson (J. Franklin Inst. 1907, **164**, 375), explains also the ancient Egyptian method of improving bricks by means of infusions of straw, as mentioned in Exodus, v. (Acheson, J.S.C.I. 1910, 29, 246.)

A further important application is the preparation of reversible metal sols by means of protalbic and lysalbic acids, two albumin decomposition products (Paal and Amberger, Ber. 1904, **37**, 124; 1907, **40**, 1392). The resulting sols may, in contrast to normal unprotected hydrophobic sols, contain high concentrations of disperse phase, and on evaporation the protected solid is left as a brittle, lustrous dark-coloured mass which disperses spontaneously in water to reform the metallic sol. Protected metal sols such as collargol are now used as mild antiseptics either externally or for intravenous injection.

OSMOTIC PRESSURE OF COLLOIDS.—Since there is experimental justification for assuming that the gas laws can be applied to colloidal systems, it should be possible to calculate osmotic pressure from the normal equation $P=RT\frac{n}{N}$, where n is the number of disperse particles per unit volume and N Avogadro's number. As the factor n is inversely proportional to the size of the particles, it is obvious that the osmotic pressure of a sol should increase with degree of dispersion. With hydrophobic sols N is large compared with n and the value of the osmotic pressure correspondingly small; thus with a typical, dialysed gold sol the osmotic pressure may be only a few mm. or cm. of water and the corresponding freezing-point depression or raising of boiling-point undetectable. Calculations of the apparent molecular weights of colloid particles by this means are rarely practicable. Osmotic pressure measurements on hydrophobic sols are further invalidated by the relatively large influence of foreign substances and especially of active electrolytes, as the value of n in the equation above represents the sum total of particles (ionic, molecular, or colloidal) present. According to the micellar theory which we have already discussed, ions are a necessary factor for the stability of colloid systems and so even when all impurities are removed by dialysis the osmotic effect is not due entirely to the colloid particles. Where allowance has been made for the ionic part of the micelle, reproducable results have been obtained in some cases. The most important work on this subject is that of W. Biltz (Z. physikal. Chem. 1910, **68**, 357) and of Duclaux (J. Chim. phys. 1909, **7**, 403), who was one of the early champions of the micelle theory. In the dialysis of hydrophobic sols the osmotic effect is often noticeable as an absorption of water within the dialyser although here again the effect may be due to electrolytes. In hydrophilic sols, the particles are usually of smaller size than those of hydrophobic sols, hence n is larger and the osmotic pressure generally measurable although still too small to make freezing-point depressions significant. The chief difficulties and inaccuracies in the interpretation of osmotic pressure results with hydrophobic colloids are the effect of electrolytes, the presence of decomposition products (of proteins, etc.), a swelling pressure due to solvation and a lack of knowledge as to the degree and uniformity of dispersion. Except in a few special cases there is no reason for supposing that the sol particles are all of the same magnitude and hence the "physical" molecular weight calculated from osmotic pressure data is only an average value.

If, as is generally the case, osmotic pressure is measured by means of a semi-permeable membrane, yet another complication may be introduced by the so-called Donnan equilibrium effects, due to uneven electrolyte distribution. This membrane equilibrium phenomenon was worked out in the first instance for true colloidal electrolytes such as congo red, one of whose ions can penetrate the membrane while the other cannot, but, as the micellar hypothesis suggests, the treatment can be extended to colloidal sols in general. If congo red sol be regarded as consisting of giant colloidal ions which are incapable of diffusing through negative congo red membrane and of equal numbers of mobile Na^+ ions, then if there is pure water on the other side of the membrane, each Na^+ ion which penetrates will cause a molecule of water to dissociate so as to provide a compensating OH^- ion, the corresponding H^+ ion tending to diffuse through the membrane, thus replacing the original Na^+ ion of the congo red. This phenomenon is known as membrane hydrolysis. If there is a solution of sodium chloride on the other side of the membrane from the congo red sol, some of the salt will diffuse through to the sol, but the concentration of sodium chloride will be less there than outside. The actual concentrations on either side of the membrane can be calculated by thermodynamical reasoning, it being assumed that the activities of the diffusible components are the same on both sides of the membrane. This unequal electrolyte distribution gives rise to a potential difference—the membrane potential—and there is an osmotic pressure difference between the two compartments. A considerable number of measurements of membrane potentials have been made which agree fairly well with the calculated results. For a full discussion of this subject, *see* Bolam, "The Donnan Equilibria," 1932.

THE SIZE AND SHAPE OF COLLOIDAL PARTICLES.—It is not possible to measure the size of a colloidal particle directly in the ultramicroscope, but an approximate measure may be made by counting the number of particles present at a given time in the field. The volume of this small portion of sol can be calculated and, knowing the concentration of the sol, it is a simple matter to determine the average size of the particles assuming that they are spherical or possess some other simple shape and that the density of the dispersed substance is the same as in the solid state. When the sol particles are too small to be seen in the ultramicroscope, Zsigmondy's nuclear method (Z. physikal. Chem. 1906, **56**, 65) may sometimes be applied. In this method advantage is taken of the fact that in the preparation of, for example, a gold sol, formation of the dispersed particles by reduction requires a finite time during which the solution is supersaturated with regard to gold. If a number of amicroscopic gold particles are added, the gold is deposited only on these nuclei, which thereby grow to a size sufficiently large to be counted in the ultramicroscope. Knowing the concentration of gold in the amicroscopic sol, it is thus possible to calculate the size of the original particles. A rough indication of the size of colloidal particles is also obtained by the use of a series of ultrafilters of different pore dimensions as already described. Many other methods have been attempted though generally with little success, but Wo. Ostwald and Quast (Kolloid-Z. 1929, **48**, 83, 156) have succeeded in calculating the size of particles of dye suspensions by a diffusion method. They were able to demonstrate the variation of particle size with the solvents used.

The normally prepared colloidal sol contains dispersed particles of widely varying size and is thus termed polydisperse, in contrast to isodisperse sols possessing particles of uniform size. Although the former is by far the most important type in practice, it is often important to prepare isodispersions for theoretical investigation. Here differential ultrafiltration is of considerable use and Zsigmondy's nuclear method can also be used in specific cases. A further method due to Odén, makes use of the fact that the greater the size of the particles the smaller is their stability and the more sensitive are they to coagulating influences. On addition of a quantity of electrolyte insufficient to coagulate the whole sol, therefore, only the larger particles are removed. By preferential coagulation Odén was able to prepare a series of sulphur sols of different particle size and properties. Perrin succeeded in separating a gum mastic sol into a number of isodispersions by centrifuging at different speeds, and in the hands of Odén and T. Svedberg, sedimentation has become by far the most important method of determining particle size and weight of colloid aggregate. This is discussed in the next section.

The shape of colloidal particles has received a good deal of study by Freundlich and his school, who find that they can generally be assigned to one of three classes, namely approximately spherical (all axes of same length), disc-shaped (platelets) (one axis much shorter than the other two), and rod-shaped (2 axes much shorter than the third). The last two types of particles are double refracting, possessing an anisotropy due to shape rather than an intrinsic molecular anisotropy. Such a particle only produces diffraction in the ultramicroscope if its length lies in the plane of vision at right angles to the incident light; otherwise it is invisible. As the sol particles are in motion the result is visible as a peculiar twinkling effect. Normally the particles are distributed irregularly throughout the liquid, but on stirring they arrange themselves with their long axes parallel to the stream lines so that streaks appear. This type of behaviour is shown by many dye suspensions, by vanadium pentoxide sol, proteins, etc. Rod and disc particles can be distinguished by means of polarised light.

Several interesting observations have been made as regards the shape of sol particles, one of which is the change of shape which often takes place on keeping ; thus the particles of a freshly precipitated ferric oxide sol are spherical, but age to discs with a corresponding change in optical and other properties ; the micelles of many other sols change from spherical to the rod shape on standing. Another property which has been explained on this basis is that of red gold sols to turn to blue during coagulation. This was at one time ascribed to aggregation, an explanation which became untenable when it was discovered that gold particles of widely different size all turned blue, although the final blue particles of one sol could be much smaller than the initial red ones of another. It has now been found that the particles of red gold sol are approximately spherical while those of the blue sol are disc-like.

There are several other properties closely connected with the shape and orientation of sol particles, amongst which may be mentioned the phenomenon of stream double refraction. Freshly prepared vanadium pentoxide sol containing spherical particles does not exhibit the property, but after a few days the liquid which gives no image when at rest between crossed Nicols, shows a bright field when stirred ; this is known as stream double refraction. The rod-like particles of a vanadium pentoxide sol may also be orientated by an electric current or a magnetic field, the rods arranging themselves in the direction of the current or of the lines of magnetic force.

X-ray diffraction methods have been applied to colloidal systems with some success. It was early found that a reversible protected gold sol when evaporated to dryness yielded a powder which was essentially crystalline, exhibiting the normal gold pattern, and later many actual sols were shown to consist of crystalline particles. It has already been stated that sols prepared by the interaction of concentrated solutions are initially amorphous, but age to crystalline, precipitates. This is a general effect, it having been shown that amorphous particles tend to result whenever formation has been very rapid or temperature, and hence molecular mobility, low. In general the disorderly arrangement of molecules which characterises truly amorphous material (in contrast to the many pseudo-amorphous or microcrystalline materials, such as charcoal) tends to disappear and is replaced by a regular crystalline lattice. Thus, most freshly precipitated metal hydroxides are truly amorphous and exhibit no X-ray diffraction pattern, but on standing for a few hours at room temperature or for a few minutes in boiling water, a characteristic pattern is developed. In fact just as solids can be crystalline or truly amorphous, so can the molecules of liquids be distributed at random, as is normally the case, or regularly orientated, as with liquid crystals.

It has been shown that many substances

normally considered amorphous such as rubber give characteristic X-ray diagrams when stretched. There is a critical temperature above which this change will not take place and which rises with the degree of stretching. *See* Weiser, "The Hydrous Oxides," 1936; Faraday Society discussion on liquid crystals (Trans. Faraday Soc. 1933, **29**, 881).

SEDIMENTATION AND THE ULTRACENTRIFUGE.—According to Stokes' law, all particles of a given size in a well-mixed suspension should fall at the same rate under the influence of gravity. Thus each size-group is deposited at a uniform rate and each decrease in the total rate of sedimentation indicates that some size-group has just completed its deposition. If the velocity of sedimentation in a liquid of known viscosity is measured, a determination of the size of the suspended particles may be made, and information obtained as to the heterogeneity of the system. Odén (Proc. Roy. Soc. Edin. 1916, **32**, 219) used an automatic device to measure the accumulation of a sedimenting suspension on the pan of an accurate balance immersed in the system (*see also* Svedberg, J. Amer. Chem. Soc. 1923, **45**, 943).

As sedimentation proceeds, the accumulation of particles on the bottom produces a local increase in osmotic pressure, resulting in a tendency to upward diffusion of the particles so that an equilibrium state is eventually set up with a gradually decreasing concentration upwards in the absence of disturbing factors such as convection currents, as was shown experimentally by Perrin for gamboge and mastic suspensions. This is similar to the molecular distribution of the earth's atmosphere, which becomes less dense at high altitudes.

These gravity observations are only applicable to coarse suspensions, but the method has been extended to highly dispersed colloidal sols by the development of Svedberg's ultracentrifuge (*see* numerous papers by Svedberg in J. Amer. Chem. Soc., *also* Kolloid-Z. 1930, **51**, 10). Refined centrifugal methods with high speeds of rotation enable the force applied to the particles to be varied so that at the maximum of 44,000 r.p.m. it is 110,000 times the force of gravity. Owing to the persistence of vision, an apparently continuous view of the sedimentation can be obtained and the process followed visually or photographically. Only a few c.c. of liquid are required for a determination, and equilibrium is established rapidly.

The apparent molecular weight of a Faraday gold sol has been shown to be about 1,300,000. Much smaller particles may be measured by means of the ultracentrifuge, and the most interesting results are those obtained for the proteins, a surprisingly large number of which, including egg and serum albumin, serum globulin, legumin, hæmocyanins, etc., are isodisperse. Polydisperse proteins include gelatin, casein, lactalbumin, fibrinogen, ovoglobulin, etc., all of which are unstable and show varying dispersity with time. Egg albumin has a molecular weight of 34,500 and other proteins have molecular weights that are multiples of this amount (Svedberg, Nature, 1929, **123**, 871). The hæmocyanins have very high molecular weights, that of *helix* hæmocyanin being 5,000,000. The ultracentrifugal method has been extended to sols which are on the borderline of true solutions, that of sodium eosinate, for example, which just begins to exhibit colloidal properties, having a molecular weight of 1,380, and even the heavy ions of cæsium can be made to form a sediment. The ultracentrifuge will certainly find increasing use in the future in spite of the high cost of installation. Its biological applications are important, it being found that viruses, etc., possess remarkably well defined ultramicroscopic size and shape.

SOME PROPERTIES OF HYDROPHILIC SOLS.—A great deal of information has been obtained from the study of the viscosity-concentration relationship in disperse systems. Einstein deduced the following expression:

$$\eta_s = \eta_0 (1 + 2{\cdot}5\phi)$$

where η_s is the viscosity of the system, η_0 of the continuous phase, and ϕ the proportion by volume of the disperse phase. The viscosity should thus vary linearly with the concentration of the sol and be independent of particle size. For mechanical suspensions, Einstein's law is obeyed fairly well, but for hydrophobic sols the rise in viscosity is greater than that which the equation predicts, probably indicating that the factor ϕ has, owing to hydration, adsorption, etc., a higher value than the volume of the actual substance dispersed. The viscosity of hydrophilic sols is much greater than that of the hydrophobic sols. If Einstein's law is to hold, the volume of the disperse phase in such a system must be enormously greater than that of the dry colloid. This is one of the strongest arguments in favour of the solvation theory of lyophilic colloids which has already been discussed. When the dry lyophilic colloid is placed in the dispersion medium (*e.g.* gelatine in water) it commences to swell to several times its original volume by taking up water. Such a swollen gel then disperses directly in water if the temperature is raised, the viscosity of the sol generally increasing for some time afterwards, indicating that solvation is still taking place. To account for these facts it is assumed that the total volume of disperse phase has increased many, and in some cases several hundred, times; many substances (*e.g.* agar) in concentrations of less than 1% can take up the whole of the dispersion medium to form pseudo-solid gels. This hydration is not entirely due to direct attachment by the colloid molecules; a large part of it consists in the entrainment and immobilisation of molecules of dispersion medium by intertwining crystals and filaments of the gel substance. On the addition of electrolytes to hydrophilic sols, the first small amounts which also neutralise the charge decrease the viscosity considerably; further quantities have little effect. The surface tension of water is generally lowered by the dispersion in it of hydrophilic colloids.

Hydrophilic colloids may, under certain circumstances, be induced to separate into two immiscible liquid phases, each of which contains a different concentration of disperse phase—a phenomenon discovered by de Jong and Kruyt (Kolloid-Z. 1930, **50**, 39) and termed by them *coacervation.* This happens, for example, on the addition of alcohol or other organic or inorganic liquids to protein sols at 50°. As in the case of flocculation, a decrease in charge and in hydration is necessary to effect coacervation ; the phenomenon is not readily treated from phase rule considerations. Coacervation has considerable biological significance. *See* Bunenberg de Jong, "La Coacervation, les Coacervates et leur Importance en Biologie," Actualités scientifiques et industrielles, Paris, 1936.

Sol-Gel Transformation.—In the broadest sense, a *gel* is a substance formed by coagulation of a sol, but the term is often restricted to the transparent or opalescent continuous jellies which are formed by the cooling or evaporation of substances such as agar or gelatine, discontinuous gelatinous precipitates such as those of the metallic hydroxides being termed *coagels*. It is probable that the distinction between the two types is not fundamental and that in the latter case gelation is initially uniform, for by choosing the correct conditions, uniform jellies of ferric hydroxide, manganese dioxide, etc., can be prepared which, like silica gel, are produced by coagulation of the sol.

The hydrophilic colloids behave in very varying fashion as regards gelation. Thus gelatine and agar, which are chemically very different (the former being a protein, the latter a complex carbohydrate), both set to gels on cooling ; albumin sols do not do this, yet they are irreversibly coagulated on heating to 60° (cooking of eggs). Still another type of behaviour is shown by a dispersion of cellulose nitrate in benzene and amyl acetate, which sets to a reversible gel when the temperature is *raised* to 70°. In the gelation of hydrophilic colloids of the gelatine type, the temperatures of setting and melting may be widely separated ; this *hysteresis* in the case of agar is as much as 45°. Melting and setting temperatures tend to approach one another when increasing time is allowed for gelation. Gelation is usually preceded by a great increase in the viscosity of the sol and, as there is no break in the viscosity curve, it is generally assumed that the process, unlike crystallisation, is continuous. It may be, however, that the normal increase in viscosity with temperature decrease, combined with the elastic effects which come into play as the gel is formed, may mask any discontinuity. An experimental indication of discontinuity has been noticed by Hatschek (Kolloid-Z. 1929, **49**, 244) who found that gas bubbles in a setting sol, which are originally spherical, suddenly become lenticular.

There has been an attempt to explain the properties of gels on the assumption of their being homogeneous, one-phase systems ; this hypothesis has the support of Loeb, Pauli, and Porter, but is not wholly satisfactory. In a recent paper, Hatschek (Trans. Faraday Soc. 1936, **32**, 787) has shown that the colour of gelatine gels containing cobalt chloride changes from pink to blue on drying, when the water content of the gel is still 30%. Gels containing this amount of water or less form no ice on freezing, so it may be concluded that this percentage of water is chemically held, the rest mechanically retained. Further evidence against the one-phase gel theory comes from the ultramicroscopic resolution of many such systems.

The results of modern research tend to the conclusion that the gel substance consists of submicroscopic fibrils or threads which may be either solid or viscous liquid, amorphous or crystalline in structure, and which are formed by partial coalescence of the highly solvated hydrophilic particles which thereby enmesh relatively large amounts of the dispersion medium. According to this viewpoint there is no phase reversal on gelation, the dispersion medium remaining the continuous phase and the fact that electrolytes diffuse in dilute gels as readily as in pure water becomes easily understandable.

Some interesting work by de Jong (Z. physikal. Chem. 1927, **130**, 205) supports the flocculation theory of gelation but shows that the electric charge and hydration of an agar gel are practically the same as that of the sol. The hypothesis has been developed that charge and hydration are not uniformly distributed on the surface of the dispersed material, but are collected in strongly protected or hydrophilic regions, leaving unprotected or hydrophobic centres at which coagulation takes place. Protected portions of the surface are thus left to form the walls of the capillaries of the resulting porous aggregates. It is also postulated that on lowering the temperatures of a sol, a surface re-arrangement takes place, which results in an increased number of hydrophobic centres.

Gelation is a partial coagulation ; the process normally continues in the gel, the spongy walls adhering to one another at an increasingly large number of spots, the gel thereby shrinking and squeezing out the water enmeshed in the capillaries. This spontaneous shrinkage of a gel accompanied by exudation of liquid was noted by Graham and termed by him *syneresis*. Some gels such as silica gel show increased syneresis with rising concentration, while others (gelatine, agar, dyes, etc.) behave in the opposite manner.

It has already been stated that when a hydrophilic substance is placed in water, it swells owing to hydration. The phenomenon of swelling has been erroneously described as the reverse of syneresis, but the former is due to the taking up of bound water, the latter to the liberation of mechanically held water. While in syneresis the volume of gel+water remains constant, swelling is accompanied by a decrease in total volume, probably due to orientation of the adsorbed water molecules resulting in a closer packing than the random distribution in the normal liquid state. During the swelling of a hydrophilic colloid considerable pressure is produced ; this is probably an important factor in the growth of plants.

The effect of electrolytes on the swelling of hydrogels is very marked, different salts behaving according to the position of the anion in the lyotropic series ; thus citrates, tartrates, and sulphates lessen the amount of swelling of gelatine while thiocyanates and iodides increase it to such an extent that the gel disperses readily at room temperature. Swelling is usually at a minimum at the isoelectric point, both hydroxyl and hydrogen ions favouring the effect.

Gels are often classified as elastic or rigid, gelatine being a representative of the former and silica gel of the latter type. The distinction is really one of degree, for although gelatine is distinctly more elastic than silica, the latter vibrates to give a musical note when the containing vessel is struck.

A peculiar gel-sol transformation which has been much studied of late years by Freundlich and his collaborators, and termed by him *thixotropy*, is the " liquefaction " of gels by vigorous shaking, agitation, ultrasonic waves, etc. On laying the sol aside, gelation occurs once more, when the thixotropic effect can be repeated by shaking, etc. The rate of thixotropic solidification of gels can be increased by a suitable gentle movement which induces a mechanical coagulation of the particles ; this is termed *rheopexy*. The solidification of rheopectic substances is accelerated by ultrasonics of the type which coagulate suspensions. Thixotropy was first demonstrated with a ferric hydroxide gel and is shown also by proteins (*e.g.* gelatine, although the effect is difficult to demonstrate in this system owing to rapid re-gelation), clays, paints, emulsions and protoplasm. Even silica gel may be thixotropic under certain conditions. These effects seem to be due to the type of packing of the sol or gel particles, the shape of which plays an important part. Thixotropic sludges are much used as drilling fluids in petroleum boring, and Freundlich has demonstrated that the properties of quicksands are due to a similar effect, all the quicksands examined containing finite quantities of thixotropic clays.

The action of ultrasonic waves on disperse systems has recently received a good deal of study. Weak ultrasonics seem first to orientate the particles of suspensions or sols if these are rod- or plate-shaped. Secondly, coagulation of the coarser particles of any shape takes place by accumulation at nodes or antinodes. Higher energy ultrasonics may have dispersing effects and are capable of emulsifying liquids, liquefying thixotropic gels, etc. ; this is ascribed to the collapse of cavitation in the liquids.

THE DISPERSE PHASE RULE.—A great deal of work has been devoted recently to the study of equilibria between gels and other colloidal solids and the dispersion medium. Although the solubility of a crystalloid in water is independent of the total amount present, this is not true of the dispersion of colloidal substances. In general the amount of solid substance dispersed or peptised varies with the amount of solid phase present, reaching a maximum for medium quantities. This relationship was termed by Wo. Ostwald the " Bodenkörperregel," generally translated as solid-phase rule, but as it is applicable also to disperse systems where the discontinuous phase is not solid, disperse-phase rule is a more suitable name.

Excellent obedience of this rule is shown by many dyes (*cf.* acid dyes and the solid-phase rule, Wo. Ostwald, Kolloid-Z. 1936, **76**, 291), the " solubility " of which increases to a maximum with increasing amount of dye to a constant amount of water and then falls again as the total amount of solid still further increases.

The full significance of the disperse-phase rule is not yet realised. Several explanations in terms of adsorption have been proposed, but none are sufficiently broad to cover all the phenomena of the type. Investigation of the effect of the total amount of gelatine present on its specific swelling and spontaneous dissolution in pure water shows that variation is due to soluble impurities in the gel which dissolve in water to form a solution, the concentration of which depends on the total amount of solid present ; such solutions, as above stated, have a great influence on the degree of swelling and may explain the disperse-phase effect in this case. Although with quite pure substances it may not always hold, the disperse-phase rule is of great practical significance with the ordinary materials of industry.

Descriptions of researches on disperse-phase equilibrium will be found in the Kolloid Zeitschrift from 1927 onwards ; amongst the most important investigations of systems in which the rule holds, the following may be mentioned :

(*a*) The " dispersion " or peptisation of gels, spontaneously dispersing colloids, coarse suspensions (*e.g.* $BaSO_4$ red lead, charcoal, $CaCO_3$ in ammonia, etc.).

(*b*) The stabilisation and cataphoretic velocity of suspensions (*e.g.* the migration velocity of charcoal particles increases with increasing electrolyte concentration for a given amount of charcoal, and with increasing amount of charcoal for a constant electrolyte concentration).

(*c*) Emulsification of oils (the amount of oil emulsified by a given amount of alkali in a given volume of aqueous phase is maximum for medium amounts of oil).

(*d*) Swelling of gels.

THE EFFECT OF HYDROPHILIC COLLOIDS ON SOLUBILITY, CRYSTALLISATION, AND CHEMICAL REACTION.—It has been stated above that a protective colloid such as gelatine prevents the coagulation of hydrophobic colloids—preserves a high degree of dispersion. Gelatine might be expected to have a similar retarding effect on the aggregation of ions or molecules to form solid precipitates or crystals. In fact *autoprotection* is the inhibiting effect of hydrophilic sols on their own crystallisation, with the result that a more or less colloidal solid mass is formed ; good examples of this are given by the soap compounds and many biochemicals. It is sometimes possible, under special conditions, to obtain these substances in a crystalline form.

Gelatine and other hydrophilic sols may prevent the aggregation of molecules or dispersed particles of normally insoluble substances, thus producing an abnormally great supersaturation. This effect has been studied by Hedges and Henley, J.C.S. 1928, 2718) with lead iodide, and many examples have been noticed by the present author. Whether the supersaturation is due to the prevention of aggregation of molecules, or whether a large number of colloidal particles have been formed but not allowed to grow, is not yet clear. It is certain, however, that the solubility of substances in hydrophilic sols and gels is often abnormal.

The work of Tamman and his pupils has shown that crystallisation is essentially controlled by two factors, first the rate of aggregation and orientation of a few ions or molecules to form crystal nuclei, and secondly the rate of growth of these nuclei at the expense of the material still in solution. If the former process is quicker than the latter, the result is a mass of small crystals; if rate of crystal growth is greater than that of nuclei formation, a few large crystals are produced.

The presence of a hydrophilic sol or gel may modify either or both of these factors. First, the protective influence of the colloid may prevent growth, and result in the deposition of a mass of microscopic or colloidal crystals, or even in supersaturation. On the other hand, in a gel the crystallising solution is free from mechanical and convection disturbances and so each growing nucleus comes into contact with fresh solution slowly and regularly by means of diffusion only. In the absence of the protection effect it would be expected to find large, well-formed crystals. This is the case in silica gel which has no protecting properties, Hatschek has produced large crystals of gold by reduction of gold chloride in this medium, and Holmes has grown crystals of copper, lead iodide, etc., of considerable size. This type of crystals growth in gels has probably played a considerable part in the formation of large mineral crystals in silica rocks. Crystallisation in gels usually has the further effect of modifying the crystal habit of the substance. Very often tree-like growths, characteristic of the crystallisation of thin films, are produced. Such, for example, are the numerous varieties of lead trees and spiral crystals described by King and Stuart (J.C.S. 1938, 642). There may also be a tendency towards spherwlite formation. This rounding of crystal contours is made use of in the addition of small quantities of gelatine to ice cream with the result that no sharp crystals of ice are formed and the product is smooth to the palate. The protective action of glue on crystal growth is illustrated in practice by the action of this substance as a retarder in the setting of plaster.

A great many observations have been made on the precipitation of insoluble substances by reaction in gels. It is usual to carry out such experiments by mixing in a test tube a dilute solution of one of the reactants with the gel before solidification, and afterwards placing a more concentrated solution of the second reactant above the gel. The substance in more concentrated solution diffuses into the gel where double decomposition takes place. It might be assumed that such a method of carrying out a precipitation in the absence of mechanical and convection disturbances, where the reacting substances mix only by diffusion and the insoluble product remains where it is precipitated, would be ideal for quantitative study, but we have, unfortunately, no means of determining in what way, if at all, the gel modifies the course of the precipitation. It is found, however, that precipitation reactions in capillary tubes and in porous solids are similar to those in gels, and as chemical reaction in gels is the rule in biological systems the matter is of considerable importance.

The precipitate formed by reaction in a gel may consist of an apparently continuous mass, a limited number of large and discrete particles, a cellular structure, or a series of bands or discs of precipitate separated by clear spaces. Precipitates of the last type, known as Liesegang rings, have been widely studied and are difficult to explain by means of any one theory. For an authoritative account and bibliography of this phenomenon, *see* Hedges, " Liesegang Rings and other Periodic Structures " (1932).

INDUSTRIAL APPLICATIONS.—With the rapid growth and increasing understanding of colloid chemistry, applications of its principles are to be found in practically every branch of science and industry. As all plant and animal organisms are colloidal in character, biological, medical, and nutritional sciences have to take account of the discoveries of the colloid chemist. The colloidal properties of humus, clays, zeolites, etc., enable them, by base exchange, to hold soluble salts which would otherwise be washed out of the soil and unavailable to plants. All fibres are of organic colloid origin, and thus the textile industries are colloid industries; especially so is the manufacture of artificial silk, in which nature's colloids have to be imitated. Predominantly colloidal materials are also used or prepared in the manufacture of soaps, detergents and wetting agents; dyestuffs, films, cellophane and plastics; synthetic resins, rubber, adhesives, leather, tars, bitumen and asphalt; lubricants, horticultural sprays, paper, paints, bread, butter and margarine; glass, ceramics and cements; absorbents, decolorising media, etc., etc.

Bibliography.—Wo. Ostwald's " Theoretical and Applied Colloid Chemistry " (Wiley) is a stimulating, general introduction to the subject. Hatschek, " Colloids " (Churchill) is more detailed, and Hedges, " Colloids " (Arnold, 1931) gives a non-mathematical treatment of the subject on modern lines. Von Buzágh, " Kolloidik " (Steinkopff, Leipzig, 1936) gives a brief, systematic treatment, Bechhold, " Einfuhrung in die Lehre von den Kolloiden " (Steinkopff, 1934) is a collection of clearly-written articles by different authors, and Taylor, " Physical Chemistry," Vol. 2 (Macmillan, 1931) contains a useful section with extensive references. More comprehensive monographs include Jerome Alexander, " Colloid Chemistry, Theoretical and Applied " (1926–1935), Freundlich, " Kapillarchemie " (Akad. Verlag, Leipzig), Zsigmondy, " Kolloidchemie " (Spamer, Leipzig). Reference should also be made to the " Colloid Symposium Monographs," edited by H. B. Weiser, whose " Inorganic Colloid Chemistry," Vols. I, II and III, 1938, and to reports of the Faraday Society discussions on colloidal subjects (*e.g.* " Colloidal Electrolytes," Trans. Faraday Soc. 1935, **31**, 1; " Fogs, Smokes, etc.," *ibid.* 1936, **32**, 1042; "Polymerisation," *ibid.* 1936, **32**, 3; "Colloid Aspects of Textiles," *ibid.* 1933, **29**, 1.

A. K.

COLLOPHANITE. A colloidal hydrated phosphate and carbonate of calcium forming an important constituent of phosphorites and rock-phosphates. It is amorphous and optically isotropic, and forms concretionary masses resembling opal or gum in appearance, with a vitreous to resinous lustre and a conchoidal fracture. The material may be opaque or translucent to nearly transparent, and the colour ranges through colourless, white, yellow, brown, and reddish. An earthy variety is known as *monite*. Sp.gr. 2·69–2·77 (of monite 2·1) ; hardness 4½ ; refractive index 1·569–1·612. A. Lacroix (1910) gives the formula as

$$\begin{cases} x[\mathrm{Ca_3(PO_4)_2}]+y\mathrm{CaCO_3}+z\mathrm{H_2O} \\ x[(\mathrm{CaF})_2\mathrm{Ca_8(PO_4)_6}]+y\mathrm{CaCO_3}+z\mathrm{H_2O} \end{cases}$$

which includes also the variety called *fluocollophanite*. W. T. Schaller (1911) gives the formula as $9\mathrm{CaO}\cdot3\mathrm{P_2O_5}\cdot\mathrm{CaO}\cdot\mathrm{CO_2}\cdot\mathrm{H_2O}+n\mathrm{H_2O}$. The mineral is found in three classes of deposits : in guano deposits, having been first recognised in the guano of Sombrero, West Indies ; in pockets of phosphorites ; and in the phosphatic nodules and coprolites of sedimentary rocks ranging in age from the Eocene to the Silurian. Material of the last of these modes of occurrence frequently contains fluorine in addition to carbonate and phosphate, and is distinguished as fluocollophanite.

L. J. S.

COLLORESIN *v.* CELLULOSE PLASTICS.

COLOCYNTH. *Bitter apple. Colocynthis*, "British Pharmacopœia"; deleted from "United States Pharmacopœia," XI, 1936. (Fr. *Coloquinte* ; Ger. *Koloquinte.*)

The dried pulp of the fruit, freed from seeds, of *Citrullus Colocynthis* Schrader (Fam. Cucurbitaceæ), a prostrate perennial of the gourd family, inhabiting the warm, dry districts of the Old World—India, Persia, Arabia, Syria, and the African and European shores of the Mediterranean. It is cultivated in Spain and Cyprus. (*Cf.* Bentl. a. Trim. 114).

The "British Pharmacopœia" demands that not more than 3% of fixed oil be extracted by petroleum spirit, and that the ash be not more than 8%. The two chief varieties imported are Turkey and Spanish colocynth, of which the former is the whiter, the richer in pulp and the more esteemed.

Colocynth was well known to Greek, Roman, and Arabian medicine, and in the form of solid extract enters into many of the purgative pills of modern pharmacy. It is a drastic purgative, rarely used alone. Small quantities of the extract have sometimes proved fatal ; the powdered drug irritates mucous membranes. The purgative action is said to depend on two substances, one of which is alkaloidal ; neither has been isolated. For inactive constituents, *see* Power and Moore (J.C.S. 1910, **97**, 99).

G. B.

COLOGNE YELLOW *v.* CHROMIUM.

COLOPHONY. Colophony, or common rosin, usually termed simply *rosin*, is the residue obtained by the removal of the essential oil from the oleo-resin derived from various species of pine, chiefly *Pinus australis, P. tœda, P. pinaster*, and *P. laricio*. The principal source of supply is the United States, a certain amount coming from France and Russia. There are vast areas of pine trees in India, and there are great possibilities of development of the rosin industry there. As the trees are exhausted without equivalent afforestation in the United States, the gathering grounds spread further afield, and fresh species of pine are met with, so that the American rosin is the product of a number of species. In the United States the oleo-resin or turpentine is collected by what is known as the " box " system. The trees are " boxed " in autumn and winter, that is, excavations of characteristic shape are made in the trunks about 8 in. above the ground. These " boxes " hold from 5 to 10 lb. of the exudation. The bark is cut away for about 3 ft. above the box and the wood is scored with grooves leading to the box. The exudation commences about the following March and goes on till about the middle of October. The tapping life of the tree varies from 5 to 8 years.

In France, a different method of collection is used, known as the cups and gutter system. The production is confined to the Landes district and the pots attached to the pine trees is a familiar sight to travellers in that locality. The principal tree used is *Pinus pinaster*. The oleo-resin exudes from the tree from March to October from incisions made with an axe. This incision is known as the " carre " and is kept open by removal of a thin slice every week and is gradually extended to about 12 ft. from the ground. Small gutters made of galvanised iron are fixed so as to lead the oleo-resin into a small cup or pot nailed to the tree at a suitable point.

The tree used in India is the " chir," *Pinus longifolia*, and collection is similar to the French method. If the trees are lightly tapped in France or India they may have a tapping life of 30 to 40 years, but if they are " tapped to death " (gemmage à mort) their active life may be only 5 to 6 years, when they are felled for timber.

The oil of turpentine is distilled off from the oleo-resin, and the residual solid matter, which is melted and strained into barrels, is the ordinary rosin of commerce.

Colophony comes into the market graded according to colour. That sold under Mark A is nearly black, and numerous qualities exist until that marked W.W is " water white " rosin of the finest quality. It is a brittle substance with a glassy fracture, soluble in ether, chloroform, light petroleum, acetone and alcohol. It is soluble in most volatile and fixed oils. It softens at about 75° and is completely melted at 120°–135°. As it is the cheapest commercial resin, it is never adulterated. It consists almost entirely of a free acid or mixture of acids, partly in the form of an anhydride. The principal acid is termed abietic acid (*q.v.*). A small amount of esters may be present. The analytical characters of rosin are as follows :

Specific gravity at 15°=1·0451–1·085.
Acid value=150–175.
Ester value=7–20.
Iodine value (Hübl)=118–128.
Unsaponifiable matter=4–9%.

The iodine value determined by the Wijs process is nearly double that found by the Hübl process. The former gives very variable figures if the conditions, such as time and temperature, are varied, whereas the Hübl value is far less dependent on small changes of conditions, and is therefore the better figure for a standard, as it is for resins generally.

A useful test for rosin in other substances, such as shellac, is the Storch-Morawski reaction. About 0·1 g. of the substance is dissolved in 10 c.c. of hot acetic anhydride; the mixture is allowed to cool and a little sulphuric acid of specific gravity about 1.53, is allowed to flow down the side of the test-tube. In the presence of 1% or less of rosin, a red-violet-purple colour appears at the junction of the liquids, which spreads to the whole of the sulphuric acid layer.

An even more delicate test for colophony is one based on that originally devised by Halphen. A solution of 1 part of phenol in 2 parts of carbon tetrachloride is prepared. A very small amount of the substance to be tested, or an extract of the same with trichlorethylene, is mixed with a small amount of this solution, and the mixture placed on a white tile adjacent to but not in contact with it is placed a few drops of a freshly prepared solution of 1 c.c. of bromine in 2 c.c. of carbon tetrachloride. The bromine vapour is allowed to drift over the solution—a wave of the hand is sufficient—and in the presence of rosin a pale blue to strong violet colour appears at the edge of the spot, which slowly spreads. So little as 0·1% of rosin in a mixture can thus be detected, and with 0·5% the colour is intense. This reaction is known as the Halphen-Hicks reaction.

Rosin is used as the basis of cheap varnishes and of resinate driers in the paint and varnish industry, in the manufacture of cheap soaps, and for sizing paper. It is also used for the manufacture of rosin oil, and for most purposes for which resins are used. Its friability and lack of resistance to wear and weather in varnishes render it a poor substitute for the harder and better class resins. It is used as an adulterant of shellac.

The chemistry of colophony is a question of considerable difficulty, and cannot be said to be entirely settled yet. So much is historical, and a great deal of the older published work has been shown to be erroneous, that only the recent work which is well established need be dealt with. References, however, to some of the more interesting of the historical papers will be found below.

The complexity of the " rosin," or as they are, unfortunately, often termed " resin," acids (which name will be used here, as it has been used in so many publications), together with the fact that rosin from different pine trees contains different acids, and also that methods of treatment or so-called isolation have frequently altered the character of the acids, have made it exceedingly difficult to even compare, much less reconcile, a good deal of one observer's work with that of another.

To-day it may be said that the " pine resin acids " are all fairly closely related, in so far as they all appear to be built up on a hydrophenanthrene skeleton, and on the basis of the isoprene rule. The principal acid, which is the main constituent of American rosin, is abietic acid. This acid is found in both the dextro- and the lævo- varieties, and the two acids are probably true optical enantiomorphs—having identical structural constitutions. Of the acids known as pimaric acid, *l*-pimaric acid is closely related to abietic acid, but in what exact manner is not yet clear.

It is unfortunate that the names *l*-pimaric and *d*-pimaric acids have been retained, as *d*-pimaric acid is certainly not the optical isomeride of *l*-pimaric acid. The elucidation of the structure of abietic acid, $C_{20}H_{30}O_2$ ($C_{19}H_{29}{\cdot}COOH$), is chiefly due to Ruzicka and his associates. The same is true in regard to dextro-pimaric acid (*v.* ABIETIC ACID).

Reference may be made to the following: C. E. Soane, Bibliography (J. Oil. Col. Chem. Assoc. 1922, **5**, 320), in which everything of importance up to 1922 is quoted; Ruzicka and his colleagues (Helv. Chim. Acta, 1922 **5**, 581; 1923, **6**, 677, 1077–1096; 1925, **8**, 632–636; 1924, **7**, 875; 1927, **10**, 915; 1931, **14**, 545; 1932, **15**, 1300, 1289, 915; 1933, **16**, 169); and R. D. Haworth (J.C.S. 1932, 1784, 2248, 2717).

Bacon and Ruzicka (Chem. and Ind. 1936 **55**, 546) have now thrown some doubt on their formula for abietic acid. Recent work on *l*-pimaric acid has shown that the possibility is not excluded that conjugation does not exist in abietic acid, and that therefore the position of the double bonds may require reconsideration.

E. J. P.

"COLORADO" CRUCIBLE *v.* ASSAYING.

COLORAN B7. A highly sulphonated product of a fatty oil used as a wetting-out agent.

COLORIMETERS and COLOUR COMPARATORS. The name " colorimeter " is applied somewhat loosely to any instrument in which the observer has to arrange a colour match in a photometric field, irrespective of the kind of information which is to be derived from this colour match. Strictly, the name colorimeter should be confined to instruments designed to effect measurement of colour, that is, to provide numbers, characteristic of each colour tested, by means of which colours may be classified and their relations to one another exhibited; it should not be given to instruments in which the readings give no information about the observed colour, a colour match being used merely as a criterion for the measurement of something else, say the concentration of a solution. Instruments of this kind are better described as colour comparators. Unfortunately, the existence of well-established trade names makes it impracticable to adhere consistently to this distinction in referring to proprietary instruments, but the distinction in function should be borne in mind, and the first section of this article will deal with true colorimeters, instruments whose primary function is the quantitative study of colour *qua* colour, while the second part will deal with colour comparators, whose primary (and usually only) function is the measurement of something other than colour.

Colorimeters.—The different colour sensations which light may excite in the normal human eye arise from differences in the spectral distribution of energy in the radiation entering the eye, or, more briefly, in the spectral quality of the stimulus. The theory of the relations between the physical stimuli and the colours observed would carry us outside the scope of the present article; suffice it to say that the essential properties of stimuli which determine whether or not they will produce a visual match are found to be functions of three independent variables. Three independent numbers are necessary to specify, quantitatively, the matching properties of any stimulus, and any two stimuli, whether physically similar in spectral composition or not, which have all three numbers equal, will produce visual effects identical both in colour and brightness. This fact necessarily has its origin in some triple structure of the receiving mechanism in the eye. Little is known of the physiological cause of this triplicity, but the fundamental variables may be regarded as the degrees of stimulation of three independent sets of receptors, differing from one another in their relative sensitivities to the various parts of the spectrum. Differences in the relative degrees of stimulation of the three receptor systems are recognised as differences in colour; differences in the actual degrees of stimulation, without change in the relative degrees, are recognised as differences in intensity or brightness. Any two stimuli, whatever their spectral composition, which produce the same degrees of stimulation, both relative and actual, in the three receptors, appear identical both in colour and brightness; the eye can analyse no further.

It is not easy to ascertain the values of these fundamental variables characteristic of any stimulus. Fortunately, it is not necessary to do so in order to measure colour. If the visual values of all stimuli in terms of the three fundamental variables were known, it is obvious that merely by solving simultaneous equations these variables could be eliminated and any or all of the stimuli expressed in terms of any three of them. This shows that it is possible to express the visual properties of stimuli in terms of variables which are simply quantities of three other stimuli. This being so, it should be possible to effect direct determination of those quantities without troubling about the fundamental variables, and this is in fact done in the type of instrument now to be described.

The Trichromatic Colorimeter consists in principle of a matching field one side of which is illuminated by the stimulus being measured, the other side being illuminated by a controllable mixture of three standard stimuli, which may consist of monochromatic radiations obtained spectroscopically, or may be produced by passing white light through colour filters. If the colours of the three standard stimuli are well chosen it will be found that the great majority of other stimuli can be matched exactly by a suitable mixture of the three standards. The quantities of these standards used in any match are indicated on the scales of the instrument.

These scale readings do not, however, afford a convenient comparison of the quantities of the three standards. In comparing quantities of light of different colours it is desirable to express them in units the significance of which is independent of the peculiarities of construction of any particular instrument. Any choice of units is arbitrary, and there are numerous alternative systems from which selection could be made. In the system most widely used, because of its practical convenience, the quantities of the three standards which are required to match a standard white (*see later*) are regarded as equal. Measurements are converted to this basis by multiplying the observed scale readings by suitable numerical factors, usually termed the *white light factors*. These factors are easily obtained from the scale readings observed when matching the standard white. Quantities based on this convention are said to be expressed in *trichromatic units*. Hereafter, any reference to the scale readings of a trichromatic colorimeter will not mean the numbers directly observed on the scales of the instrument but the equivalent numbers on the trichromatic bases obtained on reduction by the white light factors.

In order to measure the colour of a specimen of material under a given illumination, which may or may not be the standard white light on which the scale factors are based; the light reflected from the specimen, if opaque, is introduced to the test field of the colorimeter and matched in colour and brightness by a suitable mixture of the instrument standards. Denoting the standards by A, B, and C, and the quantities (reduced scale readings) required to match the specimen, S, by a_s, b_s, and c_s. The quantity of the light from S present in the field of view, when evaluated on the same system as the standards, must be equal to the total quantity of the light in the comparison field, and the result of this colour match is expressed in the equation:

$$(a_s+b_s+c_s)\mathrm{S}=a_s\mathrm{A}+b_s\mathrm{B}+c_s\mathrm{C}$$

Dividing both sides by the total quantity the proportional composition of one trichromatic unit of the light from S is

$$\mathrm{S}=\alpha\mathrm{A}+\beta\mathrm{B}+\gamma\mathrm{C}$$

where $\alpha=a_s/(a_s+b_s+c_s)$, etc. The quantities α, β, and γ, whose sum is unity, are termed the *trichromatic coefficients* of S in terms of the standards A, B, and C, and the property which they define is termed the *colour-quality* of S. Colour quality as thus defined is independent of intensity. It depends on the constitution of the light and not on its amount. It is possible therefore to have materials exhibiting the same colour quality but differing in brightness. For instance, a bright yellow and a dark brown may have the same colour quality, but the former may reflect ten to twenty times as much of the incident light as the latter. Any two materials related in this way can be made to look alike by increasing the intensity of illumination of the darker specimen (or diminishing that of the lighter) until the absolute amounts of light reflected from each are equal. However, objects are not normally compared in this way; our ideas of their appearances are based on comparisons under the same intensity of illumination, and brown is therefore regarded as a different colour from yellow. In order to define the colours of materials completely we must measure not only colour quality but also the property which determines their relative brightnesses. For this purpose it is necessary to adopt a standard of comparison, and the one now adopted in standard practice is the brightness of a magnesium oxide surface, prepared by smoking a silvered plate over a magnesium flame. The brightness of this surface when illuminated at an angle of 45° and viewed normally (or vice versa) closely approximates to that of a perfectly reflecting, perfectly diffusing surface, and is given the value unity. The ratio of the brightness of any material to that of the magnesium oxide standard under the same intensity of illumination is termed the *brightness factor* of the material. In order to determine the brightness factor we utilise the same observations as for the trichromatic coefficients, but require in addition to make a similar measurement with the magnesium oxide screen in place of the specimen. Denoting the reduced scale readings for this match by a_m, b_m, and c_m, the following equation expresses the quantity equation in trichromatic units:

$$(a_m + b_m + c_m)\mathrm{M} = a_m\mathrm{A} + b_m\mathrm{B} + c_m\mathrm{C}$$

whilst for the specimen under the same illumination it was:

$$(a_s + b_s + c_s)\mathrm{S} = a_s\mathrm{A} + b_s\mathrm{B} + c_s\mathrm{C}$$

The ratio of the quantities of light reflected from the specimen and the magnesium oxide, expressed in trichromatic units, is therefore $(a_s + b_s + c_s)/(a_m + b_m + c_m)$. If brightness factors were only of interest as part of a colour measurement, this would be the most convenient way of evaluating them; but brightness factors are frequently measured by photometric methods for purposes unconnected with colorimetry, and it is desirable that they should always be evaluated on the same basis. In calculating brightness factors from colorimeter measurements it is necessary to obtain the result in ordinary photometric units. Quantities of the three standards which are equal on the trichromatic basis would not be equally bright. It is possible, however, to determine, by appropriate experiments the relative brightness, or luminosity, of trichromatic units of the three standards. If these be in the proportion $\mathrm{L_A} : \mathrm{L_B} : \mathrm{L_C}$; then it is evident that the brightness factor of the specimen expressed as a photometric ratio is:

$$(a_s\mathrm{L_A} + b_s\mathrm{L_B} + c_s\mathrm{L_C})/(a_m\mathrm{L_A} + b_m\mathrm{L_B} + c_m\mathrm{L_C})$$

The colour quality equation and the brightness factor (usually expressed as a percentage) completely define the appearance of the specimen under the kind of illumination for which the measurements are made.

If the three standard stimuli of a trichromatic colorimeter are chosen at random it will be found that although many colours can be matched by suitable mixtures of the standards there are others which cannot. This applies to every possible set of standards, but by a suitable choice it is possible to secure that the great majority of the colours of commerce can be directly matched. For this purpose the most suitable standards are saturated colours the hues of which match the hues of the spectrum in the red at wave-length about $0{\cdot}63\mu$, in the green at wave-length about $0{\cdot}53\mu$, and in the blue at wave-length about $0{\cdot}455\mu$.

Even then, however, there are some colours which cannot be matched by any combination of the standards. In such cases it is always possible by adding some one of the standards to the colour under test to obtain a modified colour which can be matched by the other two. The result of this process, when the various quantities are all collected to the appropriate sides of the equation, is to give an expression for the colour quality of the specimen in which one of the trichromatic coefficients has a negative sign, for example,

$$\mathrm{S} = \alpha\mathrm{A} - \beta\mathrm{B} + \gamma\mathrm{C},$$

where $\alpha - \beta + \gamma = 1$.

In order to meet such cases and render the instrument universally applicable, it is necessary in constructing a trichromatic colorimeter to make provision for throwing light of any of the three standard colours into the side of the field normally occupied by the test colour alone. Failure to make this provision in the early instruments greatly restricted their utility and prevented them from becoming widely used for scientific or industrial purposes.

The fact that the three instrumental standards are always red, green and blue has given rise to a popular belief that red, green and blue are *primary* colours, from which all others may be built up. As has been seen, this is an erroneous supposition; there are no three colours from which all others can be produced, though red, green and blue in combination can match a very large proportion of the colours of material objects. A secondary consequence of the general use of red, green and blue standards is that it is customary to denote them in colour quality equations by R, G, and B, instead of by the more general symbols here used.

For many years the only universal trichromatic colorimeter obtainable commercially has been the *Guild colorimeter* (J. Guild, Trans. Opt. Soc. 1925–26, XXVII, 106). In this instrument the three standards are obtained by passing light from an opal-bulb gas-filled lamp through specially selected red, green and blue filters fitted in annular openings provided with adjustable shutters by which the effective length of each opening can be controlled. The light transmitted by these openings is gathered by a rapidly rotating periscopic prism which combines the three coloured beams on the axis of the optical system associated with the matching field. When the speed of rotation is sufficiently rapid, flicker disappears, and a steady field is observed. Its colour is a mixture of the three standards. The relative amounts of red, green and blue in the mixed stimulus are proportional to the lengths of the corresponding apertures, and are read from scales attached to each shutter. Fig. 1 is a diagrammatic view of the essential parts of this colorimeter. CD is the periscopic prism which rotates about the optic axis DE, along which ultimately passes the light collected by the peripheral end of the periscope as it rotates past the annular windows shown in the end view, Fig. 1*a*. The specimen under test is mounted at S. Light from it enters the window I and passes through an oblique plate of clear glass J to the matching cube F. The field of view provided by this cube is a square subtending about 2° at the observation pupil H, and divided into two horizontal portions, one of which is illuminated by the beam from S, while the other contains the matching stimulus. The transparent plate J, which crosses the test beam, serves to superimpose on this beam some additional light of the same colour as the red, green or blue standard, which may be required, as already indicated, when measuring a colour one of whose trichromatic coefficients is negative. This light is collected by the right-angled prism L, passes to M, which reflects it through a small aperture in the wall of the instrument to the lens K and plate J, at which part of it is reflected along the same path as the beam from the specimen S. Between the prism M and the aperture can be fitted one of three filters similar to those used for the standards. The light superposed on the test field can thus be given the colour of any one of the standards. An annular photometric wedge N serves to adjust the intensity of the beam to the required amount. This wedge and also the three main shutters are operated by control knobs outside the instrument.

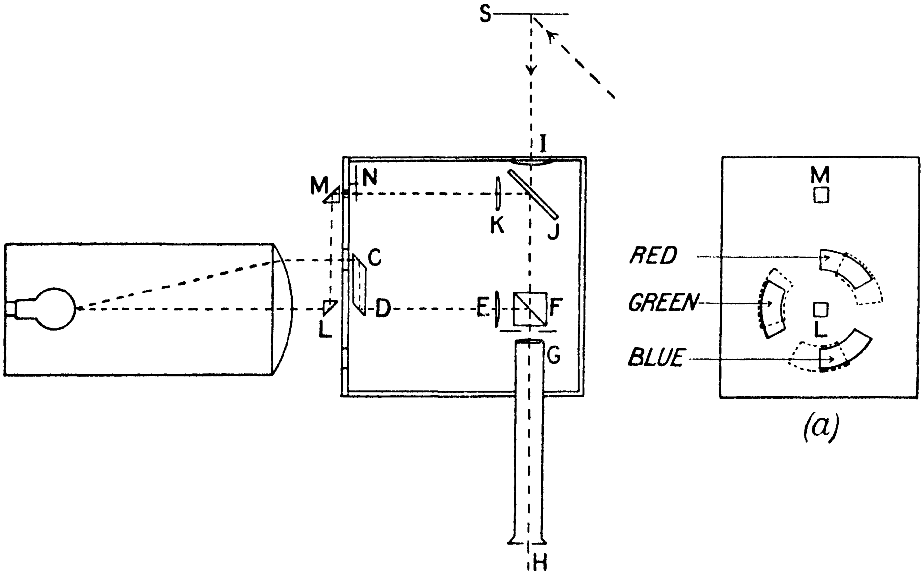


Fig. 1.

Recently another trichromatic colorimeter, designed by R. Donaldson (Proc. Physical Soc. 1935, **47**, 1068), has been placed on the market. The principles of operation are the same as in the Guild instrument, the main difference in design being in the method of mixing the three standard colours. In the Donaldson colorimeter the light entering by the three coloured apertures is concentrated by a large condensing lens in a small opening in the side of a hollow sphere, the inner surface of which is coated with magnesium oxide. The colours are thoroughly mixed by the multiple reflections to and fro inside the sphere, and light from a small region of the surface, remote from the direct unmixed beams, is directed by a suitable optical system to the matching field. This instrument has the advantage that there are no motor-driven parts. It is therefore silent in action and can be built on a lighter and more compact scale. The provision for determining negative coefficients, and the auxiliary equipment generally, are on the same lines as the corresponding features of the Guild instrument.

Manfred Richter (Z. Technische Physik. 1938, **19**, 98) has described another trichromatic colorimeter which in principle is identical with the Donaldson instrument.

A trichromatic colorimeter in which the three standard stimuli consist of monochromatic radiations isolated spectroscopically has been constructed by W. D. Wright (Trans. Opt. Soc. 1927–28, **29**, 225). This type of instrument has the advantages for some kinds of visual research that the standards are more directly defined in simple physical terms than standards obtained with colour filters and, also, there is less compensation of certain types of visual abnormality, a point of importance when the object of the work may be to reveal and study these abnormalities. This last feature is, however, a disadvantage in applied colorimetry, where it is desirable to eliminate as far as may be practicable the visual peculiarities of the observer. For this class of work instruments with filter standards are preferable. They provide better compensation of minor visual abnormalities in the majority of practical cases and are on the whole less liable to give trouble in the hands of semi-skilled observers.

The trichromatic colorimeter, in one form or another, is the fundamental instrument on which all colour measurement is based. It alone makes direct use of the three-fold relation between the physical stimulus and the observed colour imposed by the characteristics of human vision. The great generality of the method has, however, stood in the way of its adoption for industrial purposes until quite recent years. The fact that a colorimeter could be constructed with any three colours as standards and that no two instruments were ever made alike in this respect meant that results obtained on one instrument were not comparable with those obtained on another. The application of measurement to industrial needs requires that one set of standards shall be universally used. It would be unscientific, and in fact impracticable, to adopt the standards peculiar to one instrument. Fortunately, there is no need to do this.

The relations between colours exhibited by their values on any one trichromatic system necessarily originate in the relations between the excitations of the visual mechanism by the various stimuli, including the standard stimuli themselves. It follows that the values on systems with different sets of standards must be related, since the same phenomena of perception underlie them all. These relations are of a simple character and make it possible to convert colour values on any one trichromatic system to any other, and we may adopt a set of reference standards which are not necessarily incorporated in any actual instrument and convert the measurements made on any trichromatic colorimeter to this reference system. The results will then be strictly comparable with those obtained on any other trichromatic colorimeter. The theory of such transformations was first outlined by H. E. Ives (J. Franklin Inst. 1915, **180**, 673; 1923, **195**, 23), and is given more fully by Guild (Trans. Opt. Soc. 1924–25, **26**, 95, 139).

The first attempt to introduce this type of standardisation into colorimetry was made in Great Britain in 1925, when the National Physical Laboratory adopted as reference standards the three monochromatic radiations of wave-length 0·700 μ, 0·5461 μ, and 0·4358 μ. To meet the requirements of commerce, systems of measurement must have international recognition. These standards did not meet with universal approval in other countries because of the existence of negative coefficients in the expressions for some colours. As already said, this feature is common to all trichromatic systems with real colour standards. It is, however, possible to invent imaginary standards which have no real existence, but which are related to a set of real standards by relations of the same kind as those which connect two sets of real standards. By choosing suitable numerical coefficients in these relations we can define a reference system in which every real colour has all three trichromatic coefficients positive. In 1931 the Colorimetry Committee of the Commission Internationale de l'Éclairage adopted a standard system of this kind. Because the standards are not real colours, the common notation R, G, B was abandoned and replaced by X, Y, Z. The recommended symbolic form of the colour quality equation of a stimulus S on this system is

$$S = xX + yY + zZ,$$

where $x+y+z=1$. In a practical case, x, y, and z are replaced by the appropriate numerical values. The National Physical Laboratory Report on any trichromatic colorimeter submitted for test gives the constants necessary for converting measurements made with the instrument to the International reference system.

Standard scales of measurement are not in themselves sufficient to ensure unique results for the colour of any given material. The colour of a material cannot be dissociated from the quality of the illumination in which it is viewed. Most coloured objects appear different in daylight and artificial light. The kind of illumination must be specified for every colour measurement. Usually the term colour means colour by daylight, and comments, such as "Purple objects look red in lamplight," are accepted as reasonable because to most people a purple object is one which has that colour by daylight. This is regarded as the real colour of the object and its appearance in another kind of illumination, though it is just as real, is regarded as misleading.

For ordinary purposes of classification colours are measured as seen in daylight. Daylight is not, however, a satisfactory light for use in colorimetry; it is neither sufficiently constant in intensity nor in colour. Artificial sources of definite and reproducible spectral composition are required. Further, one such illuminant is not regarded as sufficient to meet the requirements of commerce, and the Commission Internationale has established three, which are designated standard illuminants A, B, and C. The first of these is simply a gas-filled lamp operated at a colour temperature of 2,848°K., and is to be used for the colorimetry of materials intended principally for use indoors in artificial light. The second and third are obtained by combining with this lamp one or other of two blue filters consisting of suitable salts in solution in glass containers. Illuminants B and C are similar in spectral constitution to two typical grades of daylight, one rather yellower and the other rather bluer than the average in this country. For the commercial colorimetry of materials whichever of these three illuminants is most likely to be appropriate should be used, and whichever is used should be specified. Of course, for special purposes, special kinds of illuminant may be called for.

The colours of many materials also depend to a considerable extent on the angle of incidence of the light and the angle from which they are viewed. Here again, special cases call for special treatment, but it is desirable to have standard conditions which may be assumed to hold unless otherwise stated. The Commission's recommendation is that specimens shall be illuminated at 45° to the surface and viewed normally to the surface. Where the peculiar nature of a material or the nature of a problem under investigation requires departure from these conditions, those actually employed should be stated.

When all conditions of measurement have been specified, there is still uncertainty in colour measurement arising from the variations of colour vision of observers. Despite statements which have been made to the contrary, any marked abnormality of vision is easily detected, and no person with serious defects of colour vision should be employed in colorimetry. There are, however, minor differences in colour vision among observers who cannot be classed as defective, and these cause systematic differences in their measurements. One great advantage of the trichromatic method of colorimetry is that when the instruments are used in the proper manner there is considerable compensation of such systematic errors in the majority of practical cases, and the results are much less dependent on the observer than is generally supposed. Nevertheless, differences exist which, if not corrected, would seriously limit the utility of colour standardisation. In addition to the other standards a standard observer is also required, and the Commission has defined such an observer by means of tables showing the results which he would obtain if he measured the various colours of the spectrum. These are based on tables prepared by Guild (Phil. Trans. 1931, **230**, A, 149) from measurements made by a number of observers in investigations conducted separately by him and by W. D. Wright (Trans. Opt. Soc. 1928–29, **30**, 141). By means of these tables it is possible to calculate the colorimetric values which would be obtained by the standard observer for any stimulus of known spectral energy distribution. In suitable cases, therefore, the standard values can be obtained for a specimen by calculation. By having a few standard specimens of various colours calibrated in this way an actual observer, by measuring these specimens, can determine the nature and magnitude of the corrections which his observations require.

From the economical point of view it is not feasible to use this method of calculation in all cases and dispense with direct measurement on colorimeters. The spectrophotometric measurements required for the indirect method must be made with great accuracy, and if carried out on the usual types of equipment, these measurements, and the subsequent lengthy calculations, occupy a time greatly in excess of that required for a colorimetric measurement. For routine work the cost is prohibitive and the method can only be profitably employed for standardisation purposes. A. C. Hardy (J. Opt. Soc. Amer. 1929, **18**, 96; 1935, **25**, 305) has devised an instrument for performing automatically all the operations involved in the spectrophotometric analysis of a specimen and the calculations of its colorimetric constants for any of the standard illuminants. The machine cannot be described in the space available here. Despite its extreme complexity it appears to afford a satisfactory method of applying the indirect method to routine colorimetry. Its necessarily high cost is, however, an obstacle to its widespread use, and it cannot at present be regarded as an easily available substitute for visual colorimeters.

Another line of development to which attention has been given in recent years is the substitution of the human observer by a system of photo-electric receivers. It is possible to design an instrument of this kind which will give directly the values of x, y, and z in the standard colour-quality equation of a specimen without the auxiliary calculations required when a visual colorimeter is used. The theory of such an instrument is simple and is given fully in a paper on Colorimetry and its relation to Photometry by Guild (Trans. Illuminating Engineering Soc. London, 1937, **2**, 127), but the practical difficulties are great and there is not yet any satisfactory photo-electric colorimeter on the market.

Meanwhile various instruments, whose indications consist of the responses of a photo-cell modified in spectral sensitivity by colour filters, have been put on the market as colorimeters. In every case within the writer's knowledge the claim to this title is unjustified, there being no attempt, successful or otherwise, to incorporate any of the essential properties of a colorimeter. Such apparatus is not, however, without its uses in a colour laboratory. For example, for checking the accuracy of reproduction of a colour for which the same pigment is always used, or for any other test in which identity of colour implies similarity of physical and chemical properties, the responses of a photo-cell used in conjunction with two or more colour filters provide a rapid and accurate means of determining colour equality. But if attempts with such apparatus be made to compare colours prepared from different materials, or even from the same material by different methods of treatment, the results may be most misleading. It cannot be too strongly emphasised that in order to measure colour it is not sufficient to have an instrument the readings of which vary with colour. The readings must depend *only* on colour and not on other factors. The same readings must always be obtained for colours which are visually identical irrespective of whether the spectral constitutions of the stimuli are similar or not. Further, it must never be possible for the instrument to give the same readings for colours which are not visually identical. Neither of these conditions can be fulfilled by a physical colorimeter unless the spectral sensitivity of the receiver, as modified by the various filters employed with it, is correctly related to the properties of the eye as defined by the tables constituting the standard observer. The complete recommendations of the Commission Internationale de l'Éclairage for colorimetric standardisation are given in Compte Rendu des Séances, 1931, of the Commission (Cambridge University Press), and also, together with an account of the derivation of the system and instructions for its practical application, in a paper by T. Smith and J. Guild (Trans. Opt. Soc. 1931–32, **33**, 73).

From the nature of colour-quality equations on the trichromatic system it is easy to exhibit the relations of colours by a diagram. In the equation $S=xX+yY+zZ$ we know that $x+y+z=1$, so an explicit statement of the values of any two of these coefficients implies the third and is sufficient to define the colour-quality. Colour-qualities may therefore be represented by points on a two-dimensional graph, using some pair of the trichromatic co-efficients as co-ordinates. In Fig. 2, for example, the curved line is the locus of points corresponding to the various spectral colours for the C.I.E. standard observer, using the x and y coefficients of the standard reference system. The point E, for which $x=y=\frac{1}{3}$, represents the colour-quality of an equi-energy spectrum. The point A represents the colour-quality for which $x=0{\cdot}3$, $y=0{\cdot}5$, and z (by implication)$=0{\cdot}2$. A diagram of this kind has many uses. From its geometrical properties we can determine graphically the colour resulting from the additive combination of any group of two or more colours in any proportions. Details of such calculations are given in some of the papers already quoted. The diagram is also useful for studying the changes of colour which take place during the fading of a pigment, or the variation of colour with concentration, and so on. For example, if the colour-qualities of a fugitive pigment at various times after the beginning of exposure to a fading agency be plotted and the points so obtained be joined by a continuous line, the whole course of the fading process can be seen at a glance. It is also useful in such cases to plot a graph of the brightness factor against the other variable—time of fading, concentration, etc. With some pigments the change in fading is almost entirely a change of brightness factor with little change of colour-quality; with others the reverse is the case, while with many, both the brightness and colour-quality change. This method of studying colour phenomena has been much utilised in the research laboratories of the colour industries.

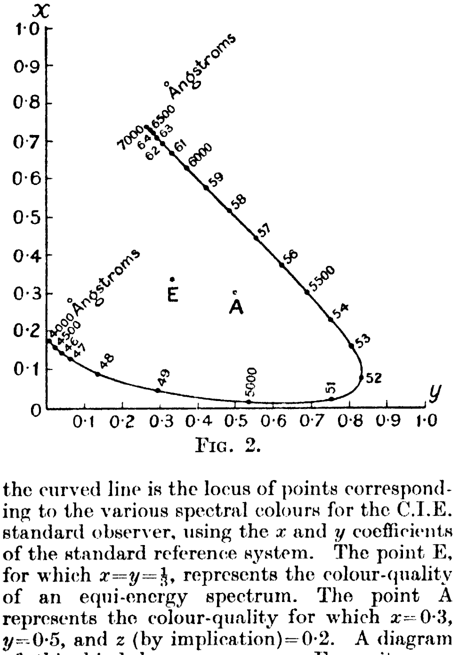


FIG. 2.

Other types of colorimeter employing the principle of additive colour mixture have been described and used for special purposes. In some of these colours are matched by mixing white light with monochromatic light of suitable wave-length, *e.g.* the colorimeters of P. G. Nutting (Bur. Stand. Bulletin, 1913, No. 9) and I. G. Prest (J. Opt. Soc. Amer. 1924, **8**, 173); in others by combining suitable pairs of monochromatic stimuli, as in the *Vector colorimeter* of Guild (Trans. Opt. Soc. 1925–26, **27**, 139), and others which have since been developed on similar principles. All such methods derive their ultimate significance from the fundamental trichromatic method, and results obtained by them can be converted to the standard trichromatic basis, and vice versa. None of these instruments is used in industry, as far as the writer is aware, and details of their construction is omitted from this article.

A somewhat different method of colour measurement, which also in principle depends on the additive mixing of standard stimuli, is employed in the Ostwald system of colorimetry. In this system a colour is expressed by the equation $C+W+B=1$, where C is the *amount of full colour*, W the *amount of white*, and B the *amount of black*, expressed as proportions, required to match the colour. The "full colours" consist of a series of colours of fairly high saturation ranging in hue from the red of the spectrum through orange, yellow, green and blue to violet, and thence through purple, magenta and cerise back to red. These colours form what Ostwald terms the chromatic circle. A mixture of one of the full colours with white produces various degrees of paleness of colour, while admixture with black reduces the brightness. Important claims are made for this system, not the least of which is that it is the only system of colour specification which takes account of the psychological and æsthetic aspects of colour. It may be stated, however, that these considerations are extraneous to the principles of colour measurement as developed in Great Britain and the United States and embodied in the international system. The subjective relations of dissimilar colours are the proper concern of the user of colour—the artist, architect, etc.—who aims at obtaining certain æsthetic effects by his manipulation of colours; but they are not the concern of the colorimetrist, who may only take account of those relations which are necessary and sufficient to provide a basis of classification fulfilling the fundamental requirements of measurement. The only subjective relation which is required, or which is permissible, is the relation involved in colour matching—that of appearing alike both in colour and brightness. For practical measurement on Ostwald's system examples of the standard *full colours* are necessary. These are generally supplied as specimens of dyed wool mounted on slides convenient for insertion in a suitable optical instrument. When the appropriate full colour has been found by trial the coefficients in the Ostwald equation have to be determined. The methods employed are somewhat complicated and are given in Part II of Ostwald's book "Colour Science," of which an English translation by J. Scott Taylor has been published by Messrs. Windsor & Newton. Equipment for colorimetry by Ostwald's method can be obtained as accessories to the Zeiss-Pulfrich photometer, to be described later in another connection.

In addition to the methods of colorimetry based on the additive combination of standard stimuli already described, colour matching can also be effected by passing white light through a number of colour filters in succession. The first filter subtracts some of the spectral constituents from the white light ; and what is left is robbed of something more by each succeeding filter, with corresponding changes of colour. This is termed the *subtractive* method of colour mixing. Colours formed in this way are in no sense a mixture of the colours of the individual filters as is the case with additive mixtures. In a trichromatic colorimeter, for example, all of the light transmitted by each filter (if a filter type of instrument is used) goes to the matching field and contributes to the colour seen there. The details of the spectral absorption of the individual filters are immaterial ; it is their colours alone which matter. With the subtractive method the colours of the individual filters are immaterial ; it is the nature of their spectral absorption curves that matter. For example, a certain blue glass and a certain yellow glass in series may transmit green light. This happens because the blue glass transmits the blue portion of the spectrum, a considerable proportion of the green, and none of the red ; while the yellow glass transmits no blue, but varying proportions of the green to red region. The only part of the spectrum which both glasses transmit is the green, and it is a common mistake to think that any blue filter and any yellow filter will give green in combination, as it would be possible to have two filters, identical in their colours with those just considered, which in combination would let through no light at all. This would be the case if the yellow filter, instead of transmitting a broad spectral region including the green and red, transmitted only yellow light confined to a narrow range of wave-length. More must be known, therefore, about filters than their individual colours before the colours of subtractive combinations can be predicted. Each filter must transmit light to varying extents over a large region of the spectrum in order that some parts may be transmitted by all of them. Filters may be found with the necessary properties, and the first successful attempt to utilise this principle for colour measurement was made by J. W. Lovibond (" Measurement of Light and Colour," Geo. Gill & Sons, London) in the instrument known as the tintometer. In this instrument the light from the specimen enters one side of the matching field while light from a white diffusing surface, after passing through various coloured glasses in series, enters the other. There are three sets of these glasses. In *appearance* they may be roughly described as red, yellow and blue, the red having a tinge of blue in it. Each set consists of a series of glasses of graded density, marked with a number proportional to the density. That is to say, the glass marked 10 should have the same colour as ten glasses marked 1, or of a glass marked 4 and one marked 6, and so on. The numbers of the different sets are so related that a combination of similarly numbered members of each set is of a neutral grey colour. In the original form of the tintometer the glasses were supplied separately and had to be selected and dropped into appropriate slots in the body of the matching instrument, which was of a simple form, having as comparison fields two rectangular slots some distance apart. The full set of glasses for use with this equipment contained 155 members of each series, graded from 0·01 to 20·0, or 465 glasses in all. This degree of subdivision is superfluous, and in the most recent model of the tintometer, known as the British Drug Houses' pattern, 60 red, yellow, and blue glasses, and 12 neutrals are supplied. These are fitted in sliding frames in a matching instrument, which has the comparison fields juxtaposed, giving greater accuracy of matching than the older models. In using the tintometer an attempt is made to match the light from the specimen by a suitable combination of red, yellow and blue standards interposed in the beam from the standard white plate. If the brightness factor of the specimen is not too great this can be accomplished. If the specimen is too bright to be matched in this way, neutral glasses are inserted in the beam from the specimen, the density being increased until it is possible to effect a match with a combination of two standards in the other beam. The method of reduction of observations recommended by the makers is based on the following considerations. Any combination of red and yellow glasses alone produces hues intermediate between red and yellow, passing through orange-red, orange and yellow-orange. Combinations of yellow and blue pass through yellow-green, green and green-blue, while combinations of red and blue pass through red-violet, violet and blue-violet. Suppose a specimen matched by 6·0 red, 12·0 yellow and 1·5 blue. The smallest of these numbers is first subtracted from all, giving the result as 1·5 plus 4·5 red plus 10·5 yellow. The 4·5 red is then associated with an equal amount of the yellow, yielding the resultant 4·5 units of orange, and, as the final designation of the colour, 1·5 neutral plus 4·5 orange plus 6·0 yellow is obtained. If, on the other hand, it is necessary to darken the specimen with, say, 0·03 neutral, and that this is matched by 4·5 red and 3·5 blue, the 0·03 units of neutral tint are listed separately as *brightness* while the colour on the other side is analysed as 3·5 violet and 1·0 blue.

In the latest model of the tintometer the brightness adjustment is effected independently of the Lovibond glasses. This enables the colour match to be made with glasses from not more than two of the three series and eliminates the use of neutral glasses. This modification greatly increases the facility and accuracy of the measurement. The illuminant provided is the C.I.E. standard B, and the direction of illumination and observation are also those recommended by the Commission. Any measurement made with this instrument can, of course, be converted to the C.I.E. trichromatic system by calculations based on the spectral absorption of the Lovibond glasses. The necessary calculations may be made once and for all, and the results incorporated in charts from which corresponding values on the two systems may be read directly. Such charts have now been prepared by the makers.

Many special models of the tintometer for limited purposes are also made. These are supplied with a small number of standard glasses specially adapted for the purpose on hand, such, for instance, as the measurement of X-ray dosage by the Sabouraud-Noire pastille method; the acid washing tests of coal tar fractions; the tests of petroleums and lubricating oils; the evaluation of vitamin-content of cod-liver oil; or Nessler's ammonia test, and many others. It is probably in these restricted forms, where, owing to the small range of glasses required, the apparatus can be supplied at a much lower price and in more compact form than any universal colorimeter, that the tintometer is most widely used. The degree of reproducibility of different sets of Lovibond glasses, though by no means so good as is sometimes claimed, is nevertheless fairly satisfactory. Any Lovibond measurement can be converted to the C.I.E. trichromatic system by calculations based on the spectral absorption characterising the glasses.

In the *Eastman colorimeter*, devised by L. A. Jones (J. Opt. Soc. Amer. 1920, **4**, 420), the same principle of colour measurement is employed. The graduated series of coloured glasses used in the tintometer are here replaced by three coloured wedges which vary in density from one end to the other. The absorptive properties of the wedges are similar to those of the red, yellow and blue series of Lovibond glasses.

In concluding this brief account of colour-measuring apparatus and the principles on which they operate, it must be insisted that the successful application of colorimetry to the problems of industry is impossible without adherence to a rigorous system of standardisation as regards conditions of test, and the form in which results are expressed. The degree of standardisation effected by the Commission Internationale de l'Éclairage, though not yet perfect, embodies the pooled experience of the standardising laboratories of the principal industrial nations. Their recommendations constitute a necessary minimum, and should be strictly followed by everyone employing colorimetric methods in industry. New instruments should not be adopted because of ease of manipulation or precision of repetition unless they are designed to work under the standard conditions of the C.I.E., and unless it is possible, by suitable methods of conversion, to express any result obtained with them on the standard reference system.

Colour Comparators.—Instruments of this class, often misnamed colorimeters, are mainly used for the estimation of substances in solution. The many specific tests of this kind to which colour comparators are applied in chemical and biochemical laboratories do not come within the scope of this article, which is concerned only with instruments and the principles of their use. One of the simplest devices for work of this kind is merely a series of test-tubes containing solutions of known and graded concentrations of the substance to be estimated. The solution of unknown concentration is put in a similar test-tube and visually compared with the tubes of known concentration until that nearest to it in colour is found. This method is capable of surprisingly good results if the standard solutions are suitably graded and is still used in many laboratories. Nevertheless, more precise results are to be expected if an optical comparator is used, and such instruments have been designed. Many of the earlier forms were of crude design, and it is doubtful if they effected an increase in accuracy sufficient to compensate for the extra complexity of technique. Omitting an historical résumé, only typical instruments illustrating the various principles which are employed for chemical estimations by colour or an equivalent criterion at the present time will be described.

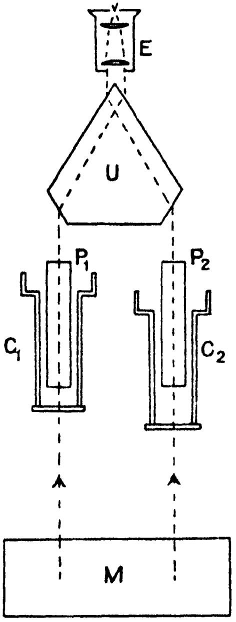


Fig. 3.

Probably the best known instrument is the *Duboscq colorimeter*, which is based on a principle also used in instruments by Patterson (J.S.C.I. 1890, **9**, 36) and Schreiner (J. Amer. Chem. Soc. 1905, **27**, 1192). Fig. 3 is a diagram of the optical system used in a modern model of the Duboscq instrument. E is an eyepiece, focussed on the sharp edge of a Ulbricht-prism U, which consists of the major portion of a rhomb of clear glass. P_1 and P_2 are "plungers" consisting of glass rods with plane polished ends. These dip into cups C_1 and C_2, the lower ends of which are plane-parallel glass plates. The plungers are fixed but the cups can be independently moved up and down by rack and pinion adjustments, scales being provided which indicate the distance from the bottom of each cup to the end of the plunger which it surrounds. M is a mirror, inclined to the plane of the diagram, which throws light vertically upwards. The beams passing through the cups and plungers follow the directions indicated by the broken lines, and illuminate the two halves of the field of view, which are sharply divided by the top edge of the Ulbricht rhomb. When both cups are empty the light losses in the two paths are equal, so if the illumination is properly adjusted the two fields will appear equally bright and the dividing line should be nearly invisible. A solution of known concentration is put in one cup, which is adjusted until the length of liquid column traversed by the light has some convenient value. The solution of unknown concentration is put in the other cup, which is racked up or down until the two fields exactly match in colour. If the unknown concentration is the same as that of the standard the match will occur when the liquid columns are of equal length. If the concentrations differ the lengths will differ and the unknown concentration is deduced from that of the standard by assuming Beer's law that for a given colour the product of the concentration and the thickness of the absorbing layer is constant. This, the normal method of using the colorimeter, requires the preparation of standard solutions of the test substance. If these are unstable, they must be frequently renewed. To obviate this need more permanent standards for various colorimetric estimations may be made from coloured glass, or from solutions of some other substance, having the same colour as a specified concentration of the test substance. Such standards may differ in their spectral absorption curve from that of the test substance, in which case the colour match will depend on the observer's colour vision and on the spectral quality of the illumination. Difficulties from the latter cause may be avoided by preparing and using the standards with an illumination of definite spectral energy distribution, one of the C.I.E. standards, for example. Standard illuminant B will give more sensitive colour discrimination for the majority of estimations than either A or C.

In cases where the test solution does not accurately obey Beer's law, there may be an advantage in using standard solutions of some other substance, even when this is not dictated by other considerations. If a standard solution of suitable colour can be prepared from constituents which do obey the law, we can reverse the usual procedure and vary the depth of the standard solution, maintaining a fixed specified depth for the test solution.

The *Autenrieth-Königsberger colorimeter* (Chem. Zentr. 1910, **1**, 2032) operates on the same principle as the Duboscq, though the matching arrangements are quite different. Light enters the instrument by two horizontal slits. Behind one of these is a parallel-sided glass cell containing the test solution, and behind the other a long wedge-shaped cell containing the standard solution. The wedge cell can be moved past the slit by a rack and pinion adjustment, a scale indicating the thickness of liquid traversed by the beam. The two beams are brought together by a suitable optical system to illuminate the two halves of the matching field. Beer's law, applied to the standard solution, provides the relation between colour, concentration, and thickness from which the result is deduced. Here also, if the standard is of different material from the test solution, Beer's law need only be true for the standard and not necessarily for the test solution.

An alternative method of visual estimation, which has the advantage of requiring no standard solutions except for the initial calibration of the apparatus, employs instead of a colour match a brightness match in approximately monochromatic light. The colorimeter of van den Bergh and Grotepass is similar in design to the Duboscq except that a single rack and pinion adjustment moves both cups simultaneously, maintaining both liquid columns of equal depth. One cup is filled with the test solution and the other with the pure solvent. A rotatable disc carrying five neutral filters made from gauze of known transparency is fitted in the path of the beam which traverses the solvent, and above the eyepiece another disc carries eight colour filters transmitting only small spectral regions. The depth of the liquid columns is brought to some predetermined value, and the colour filter whose band of transmission is nearest that part of the spectrum for which the absorption of the test solution is greatest is brought over the eyepiece. The fields now appear of the same colour but differ in brightness. The various gauze filters are inserted in the comparison side until one is found which gives the closest approximation to a brightness match. Any residual difference in brightness is removed by a small adjustment of the depth of the liquid columns. It will be observed that this method eliminates the absorption of the solvent as both beams always traverse the same thickness of liquid. The relative sensitivity of these methods depends on the nature of the spectral absorption of the test substance. In some cases a colour match gives the more sensitive criterion of concentration and in others the monochromatic brightness match. It is useful to be able to apply whichever of these methods is more sensitive in any given case, and a Duboscq or Autenrieth colorimeter can be used by the second method with the aid of a set of colour filters and a series of neutral filters, either of gauze, as used in the van den Bergh-Grotepass instrument, or of lampblack in gelatine. The exact equality of the liquid columns maintained in that instrument, though a useful feature, is not a primary requirement, and may be achieved sufficiently closely by simultaneous independent adjustment of the cups of a Duboscq type of instrument.

The *Pulfrich photometer* ("Licht und Lampe," 1925, No. 3) or *Stupho photometer*, as it is alternatively termed, can be used for a wide variety of purposes including chemical estimations either by colour match or monochromatic brightness match. Its optical system is illustrated in Fig. 4. Two beams of light, A and A′, enter the instrument *via* the lenses L_1, L_1', and then pass through diaphragms D, D′. These diaphragms constitute the essential measuring part of the instrument. The apertures are square and can be varied in size, while still remaining centred on the two optic axes, by means of micrometer screws provided with large drums outside the box graduated to read the areas of the apertures directly. These areas determine the amounts of light which the apertures transmit. This light is collected by the field lenses L_2, L_2', and the two beams are brought together by the internally reflecting prisms P, P′, to provide uniform illumination of the two sides of the matching field formed by the biprism B, the ridge of which is focused by the eyepiece E and constitutes the dividing line. A rotatable disc (not shown) contains eight spectral colour filters any one of which, or a clear blank, may be brought into positions over the aperture F.

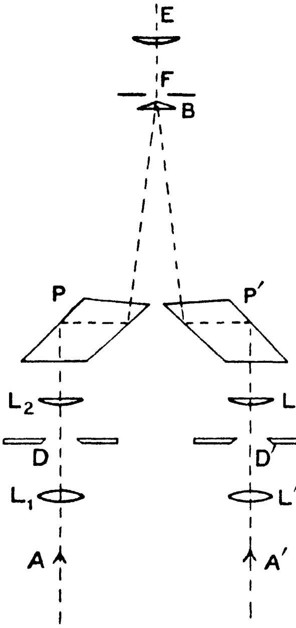


FIG. 4.

The instrument can be used either horizontally or vertically. In the latter case the light beams are directed upwards by an inclined mirror fitted to the base. For chemical estimations by colour match special cells are supplied. These consist of tubular glass walls fused to optically plane base-plates and fitted with dipping covers which give definite fluid thicknesses of 1, 10, and 50 mm., and a cell in which the thickness can be varied by a solid glass plunger which can be made to descend to various depths by rotation of the cover. The test solution is put in this cell and the standard solution in one of the invariable cells. The two fields of the photometer are made to match in intensity for white light. This can be done either by independent adjustment of the drums or by setting the drums to equal readings and adjusting the position of the illuminant until both fields are equally bright. The cells are then inserted in the beams (a suitable stage is provided) and the colour match obtained by varying the depth of the test solution as with the Duboscq colorimeter. For the monochromatic brightness method two similar cells of equal depth, respectively containing the test solution and the solvent, are used. The most suitable monochromatic filter is inserted, and the intensity of the brighter field is reduced by operating the appropriate drum until a brightness match is obtained.

Accessory attachments for various other types of measurement can be obtained for the Pulfrich photometer. Reference has been made earlier to its use in conjunction with the Ostwald colour standards. Description of these other functions of the instrument would, however, be outside the scope of this article.

The monochromatic brightness matching method of estimation clearly reduces to a determination of the ratio of the transmissions of a specified thickness of the test solution and of the pure solvent for approximately monochromatic light within a selected wavelength range determined by the filter used. The method lends itself readily to accomplishment by purely physical means. An extremely simple method is to employ a photoelectric-cell, of the rectifier type commonly used as photographic exposure meters, and a quick-response galvanometer having a steady and reproducible zero. Cells containing the solution under test and the solvent are placed in succession in the path of a beam of light from a small gas-filled lamp, such as a 50-watt motor car headlight lamp. The appropriate member of a set of spectrum filters is also inserted in the beam. The relative transmissions of the test solution and solvent for this light may be deduced from the ratio of the galvanometer deflections obtained. If care is taken to arrange the optical system so that the beam passing through the liquids is approximately collimated, and is not obstructed or scattered by the walls of the liquid cells, and so that the beam falling on the surfaces of the receiver is not displaced on interchanging the cells, very satisfactory results can be obtained.

Photo-cells of the kind mentioned require no batteries or auxiliary electrical equipment. Various types differ greatly in spectral response. For this purpose those with selenium surfaces are best, as they have a fairly good response throughout the visible spectrum. Compact self-contained colour comparators employing rectifier photo-cells are now sold by several British makers; *see* article on Optical Instruments shown at the twenty-eighth annual exhibition of the Physical Society in January 1938 (J. Scientific Instruments, 1938, **15,** 65).

For tests of solutions the maximum absorption of which is outside the visible spectrum a rectifier cell is unsuitable. If the absorption is in the infra-red, a thermopile may be substituted for the photo-cell, and, for the ultraviolet, a photo-cell of the emission type, but a difficulty arises in the great scarcity of filters suitable for isolating narrow spectral regions in either the ultra-violet or infra-red spectra.

Moll, Burger and Reichert (J. Sci. Instr. 1935, **12,** 148) have devised a "spectroscopic absorptiometer" which can be used at any part of the photographable spectrum. The essential parts are illustrated in Fig. 5. A source giving a continuous spectrum in the required spectral region is mounted about 60 cm. from the quartz lens L. The light transmitted by the lens is restricted by diaphragms to two circular beams of smaller diameter than the cells C, C′, which hold the test solution and solvent. On emerging from the cells the beams are deflected to the slit of a spectrograph by the quartz rhomboidal prisms P, P′, which are mounted one above the other. This slit is of special design, consisting of seven short slits in line. One of the beams—that through the solvent—illuminates a short slit about 0·5 mm. square. The other beam illuminates a series of six slits, each 0·5 mm. long, separated by 1 mm., and varying in width from about 0·5 mm. downwards, the width being halved at each step. Seven narrow spectra are therefore obtained at one exposure. One of these is of the light transmitted by the test solution, the other six, which vary in density in accordance with the widths of the slits, is of the light transmitted by the solvent. If at a particular wave-length the photographic density in the test spectrum is found to be the same as that in the comparison spectrum from a slit the width of which is only a quarter of that of the test slit, it can be deduced that the illumination per unit area of the comparison beam is four times as great as that of the test beam, and that the relative transmission of the solution to that of the solvent is, therefore, 25%. The use of a microphotometer for determination of plate densities is recommended. This not merely increases the accuracy of the comparison, but enables interpolation to be performed. For work in the ultra-violet a source giving a continuous ultra-violet spectrum, such as a high-intensity hydrogen lamp, must be employed. The photographic method is not nearly so convenient as visual methods, or direct-reading physical methods, but is practically the only one which can be satisfactorily used in the ultra-violet region of the spectrum.

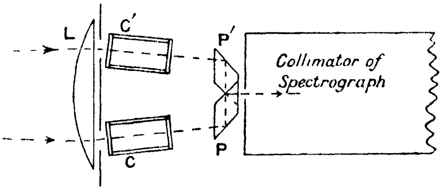


Fig. 5.

J. G.

COLOUR AND CHEMICAL CONSTITUTION. The sensation of colour is produced by the action on the retina of the eye of some portion of white light which has been scattered through the agency of a medium by which the light has been dispersed either by refraction or during transmission. Of the seventy or so octaves of the electromagnetic spectrum which have been mapped, only one, namely, that between 3,900A° and 7,600A°, represents the visible spectrum, or, in other words, the retina is only sensitive to wave-lengths within the octave. White light need not be altered in any way by reflection or transmission from or through a medium and may thereby be quite unaffected. On the other hand, certain irregularities of surface or certain properties of a solution may lead to the absorption of a portion of white light causing the rays refracted or transmitted to have colours which are complementary to those which are absorbed.

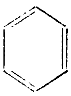
Such colour, which may be termed "physical colour" because it is produced by physical means and is entirely independent of chemical structure, is shown by a variety of natural substances, such as blue eyes, the coloured feathers of a bird, the brilliant green reflex of the wing cases of certain beetles, the colour of butterflies' wings, and of the rainbow. This type of colour can always be recognised, for example, in a bird's feather, by the fact that the colour is only produced by diffraction, and disappears when the object is viewed by transmitted light. There is, however, a type of colour which may be regarded as chemical in origin, that is to say, it is produced by intramolecular interference such as that already mentioned. It is, therefore, dependent on molecular structure, that is to say, on chemical constitution, and is the type of colour with which this article deals. This kind of colour also occurs naturally as hæmin, the colouring material of blood; as chlorophyl, the colouring matter of green grass and as most of the colours found in coloured flowers. These last can be extracted from the object in which they occur, usually as glycosides, in which the pigment is present in combination with one or more molecules of a monosaccharide.

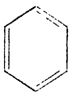
It was clearly understood that the distinction between the different kinds of colour mentioned in this article is made merely as a matter of convenience; there is, of course, no real difference between them except in the method of production. Moreover, there is no sharp division in the matter of their natural occurrence, because the feathers of certain parrots have been found to contain extractable pigments. A chemical substance appears coloured when it gives definite absorption bands in the visible region of the spectrum, the colour being compounded of the colours which remain after those represented by the absorption bands have been removed. A blue colour is given, therefore, by a substance which gives an absorption band in the red, yellow, and green—a red colour by one showing absorption in the blue end of the spectrum.

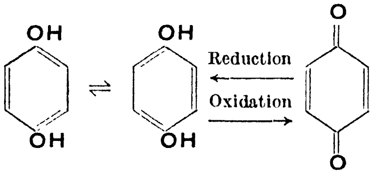
It is obvious, however, that phenomenon of this kind cannot be confined to the single octave representing the visible spectrum, but must be spread over the whole range of the electromagnetic spectrum. Unfortunately, we have no means of detecting absorption bands outside the visible region, except in the ultra-violet so far as it is susceptible to the photographic plate, and in the infra-red so far as they can be detected by heat measurements. There must, therefore, be a wide range of substances outside the visible region, which since they give no absorption in this region are apparently colourless, but on account of the fact that they give absorption outside the visible region are to be regarded as possessing "invisible" colour, or, in other words, colour that cannot be detected by the eye.

The hydrocarbon benzene (C_6H_6) is a case in point. This substance shows little absorption throughout the visible region of the spectrum, and therefore appears colourless to the eye. If, however, a photograph is taken in the ultra-violet region it is found that definite marked absorption bands occur, meaning that if the eye could detect waves in this region benzene would be strongly coloured.

It is assumed that this absorption is caused by the rhythmic interchange between the two "Kekulé" individuals I and II, which represent the formula of benzene, and accounts for its symmetrical properties as well as its stability. It is common to all derivatives in which this interchange is possible. If, however, the interchange is restricted as, for example, when benzene is oxidised to quinone, the ultra violet absorption is influenced, and the absorption thrown into the visible region of the spectrum thus producing colour. Taking, therefore, two comparable examples in hydroquinone and quinone, there is in the one the rhythmic vibration due to the benzene structure, and in the other the absence of such vibration and the occurrence of colour.


I.

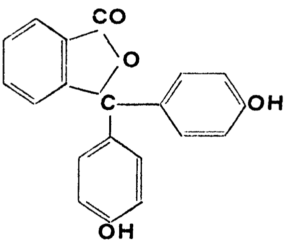

II.



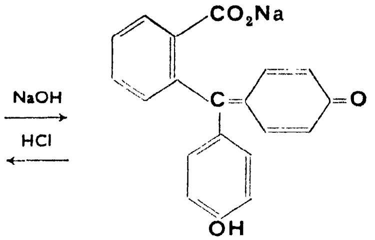
Rhythmic vibration producing ultra-violet absorption but no visible colour.

Rhythmic vibration producing absorption in the visible region of the spectrum.

Still more striking examples of this change are shown by phenolphthalein:

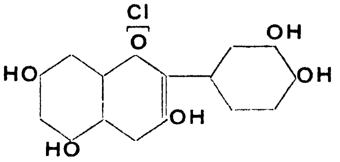


"Colourless" crystalline substance showing marked ultra-violet absorption.

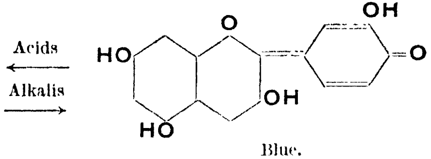


Deep red substance showing marked absorption in the visible region but diminished ultra-violet absorption.

and also by the colouring pigments of certain flowers, which may be red or blue depending on the formula of the anthocyanidin present:

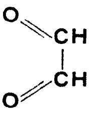


Red.

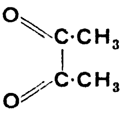


Blue.

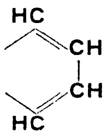
It follows, therefore, that absorption in the visible region of the spectrum, and the occurrence of visible colour, are mainly dependent on the degradation of certain forms of rhythmic vibration, and if this is true it follows that aromatic substances, that is to say, the derivatives of benzene and allied hydrocarbons in which rhythmic vibrational movement can occur, are the only substances from which compounds having visible colour can be obtained. But this is not the case, because many aliphatic substances are also visibly coloured, as, for example, diacetyl, $CH_3·CO·CO·CH_3$, glyoxal, $CHO—CHO$, and so forth. An examination of such substances shows, however, that they are all compounds having a conjugated system of double linkages, and on this account are allied to benzene:



Glyoxal.

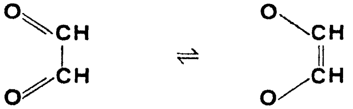


Diacetyl.

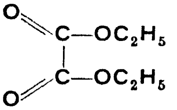


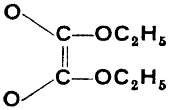
Benzene.

It is possible, therefore, that some kind of rhythmic vibration, such as that which gives rise to the ultra-violet absorption of benzene, is also present in these cases, for example:



but that the interchange, being too feeble to lead to ultra-violet absorption, shows its influence in the visible region only. Perhaps this explanation supplies a reason why certain substances which should contain the conjugated chain are colourless, for example, ethyl oxalate (I); the reason being that there is no tendency in this case for the substance to assume the tautomeric form (II), and rhythmic vibrations are therefore absent.

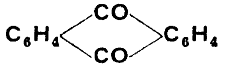
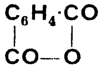
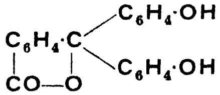

I.


II.

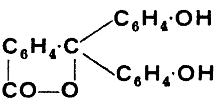
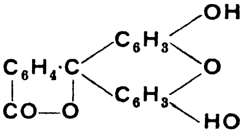
It is not proposed to deal in this article with the case of occurrence of colour in inorganic compounds. The molecular condition of these substances is so complicated that it is not possible in our present state of knowledge to envisage what may happen when a beam of white light passes through, or is reflected from, an inorganic crystal in such a way that the emerging beam is coloured. Usually the cause of colour may be ascribed to the presence of a coloured ion, such as, for example, chromium or copper, but even the molecular condition of the salts of these elements varies sufficiently to cause colourless substances to be produced from them by simple reactions. Thus, although copper sulphate is blue under normal conditions, it loses all visible colour when the five molecules of water of crystallisation are removed by heat.

General Outline.—The first synthetic dye (mauve) was produced by Sir W. H. Perkin in 1856. This branch of synthetic chemistry developed with great rapidity, and in the next twenty years the first members of many important groups of dyes had been prepared, *e.g.* fuchsin (1856), rosanilin blue (1860), and alkylated triphenylmethane dyes (1861–1866); Bismarck brown (1863), chrysoidine (1875), and naphthol orange (1876) in the azo- group; Martius yellow (1864) in the nitro- group; Magdala red (1868) in the azine series; alizarin (1869) of the anthraquinone group; fluoresceïn and eosin (1871) representing the phthaleins; and Lauth's violet (1876), foreshadowing the thiazines. By this time sufficient material had been accumulated to allow the formulation of the well-known "Witt's rule" (1876), according to which substances attained the potentiality of colour when their molecules contained certain atomic arrangements or groups, which Witt termed *chromophores*. The colour and dyeing properties were made manifest by the introduction of additional groups termed *auxochromes*.

Witt pointed out (Ber. 1876, **9**, 522) that two things are required to confer on an organic substance colour and dyeing properties. The molecule must possess a certain grouping of atoms to give it the potentiality for colour, and it must also possess a salt-forming radical to bring out the colour and dyeing properties. The atomic groupings giving the potentiality of colour he termed *chromophores*, and molecules containing them were called *chromogens*. He specified the following chromophores and gave illustrations of chromogens containing them:

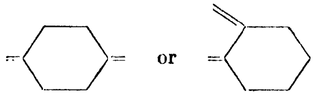
Chromophores.	Chromogens.
NO_2	$C_6H_5{\cdot}NO_2$
$—N{=}N—$	$C_6H_5—N{=}N—C_6H_5$
$—CO—$	
	

It will be noticed that some of the chromogens are colourless, *e.g.* nitrobenzene and phenolphthalein, whilst others have a feeble colour, *e.g.* azo-benzene and anthraquinone; but none of the chromogens has any dyeing property. The colour is developed or strengthened by the introduction of salt-forming radicals into the chromogens. These radicals he therefore termed *auxochromes*. Hydroxyl-, amino-, and substituted amino-groups can act as auxochromes, while sulphonic and carboxyl groups are without this function. The following table shows how the chromogens already mentioned are converted into dyes by the introduction of auxochromes:

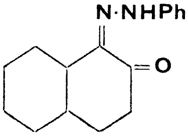
Chromogen.	Dye.
$C_6H_5NO_2$	$C_6H_4(NO_2)OH$ Nitrophenol.
	$C_6H_4(NO_2)NH_2$ Nitraniline.
$C_6H_5{-}N{=}N{-}C_6H_5$	$C_6H_5{-}N{=}N{-}C_6H_4{\cdot}OH$ Benzene-azo-phenol.
	$C_6H_5{-}N{=}N{-}C_6H_4{\cdot}NH_2$ Aniline yellow.
	 Fluorescein.

Witt's Rule is an admirable "working hypothesis" but it deals only with the connection between a coloured substance and its capacity for affixing itself to the textile fibres and leaves all questions concerning the cause of colour in the chromophore unanswered. Nor, indeed, is the "vibration hypothesis" mentioned above anything more than a reference to a physical condition which is not clearly understood.

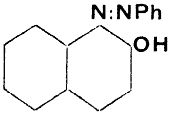
The Quinonoid and Modified Quinonoid Theories.—In 1888 (Proc. Chem. Soc. 1888, 27–33) H. E. Armstrong pointed out that the chemical formulæ of the well-known dyestuffs either contained the *quinonoid* grouping or could be slightly modified or rearranged, in accordance with accepted ideas on tautomerism, so as to contain this grouping. The *quinonoid* grouping may be defined as a benzene nucleus to which other atoms or groups are attached by double bonds in the *para-* or *ortho-* position :



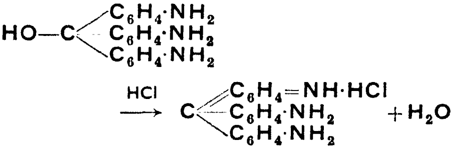
Armstrong was probably much impressed by the then recently discovered fact that benzene-azo-β-naphthol was identical with the phenyl-hydrazone of β-naphthaquinone, so that there was as much justification for the formula



as for the more usual one based on the formation of the substance from β-naphthol and a benzene-diazonium salt, viz. :



and if it were allowable to assume tautomerism to a quinonoid form in this case, it might be allowable in other cases, *e.g.* in the case of *p*-rosaniline it would be consistent to suppose that on the conversion of the base into salts there was elimination of a molecule of water and formation of a substance with a quinonoid structure :



$$HO-C\begin{cases}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{cases}\xrightarrow{HCl}C\begin{cases}C_6H_4{=}NH\cdot HCl\\C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{cases}+H_2O$$

In many cases the ordinary formula already contained the quinonoid structure.

The theory was the first real contribution to the relation between colour and constitution, because it indicated that the formation of the quinone structure was one of the influences which affected the rhythmic vibration of the Kekulé individuals of benzene so as to throw the absorption from the ultra-violet into the visible region of the spectrum. It is immaterial whether this process leads to visible colour or not, because in certain cases—a fact which has been used to disprove the theory—derivatives possessing undoubted quinone structure are colourless, meaning, of course, that in these cases the " shift " of the absorption from the ultra-violet has not been sufficient. Moreover, opponents of the " theory " have used the argument that it cannot be correct because there are coloured substances, such as azo-benzene, which do not possess a quinone structure. This criticism could, with equal force, be applied to copper sulphate. Obviously the formation of a quinone ring from a substance already containing " potential colour " may lead to the production of visible colour or may not. It was never claimed that all coloured organic compounds possessed a quinone ring, although, as a matter of fact, such a statement would not be far removed from the truth.

The literature contains many other hypotheses, which are not theories because the exceptions to them are numerous. It is evident that one cannot distinguish between substances showing absorption in the visible region and those giving absorption in the ultra violet and infra red region of the electromagnetic spectrum. The only truly colourless substance is one showing general absorption throughout the 68 or so octaves of the electromagnetic spectrum. Disturbance leading to absorption may occur in any octave although unfortunately our instruments are not sufficiently sensitive to map more than a small part of the spectrum. This is, however, a physical question and will be answered in time by the physicists.

COLUMBITE. A columbate (niobate) of iron, usually containing some manganese (" manganocolumbite ") and tantalum, the general formula being $(Fe,Mn)(Nb,Ta)_2O_6$. With an increase in the amount of tantalum, there is a transition to the isomorphous species, *tantalite.* The orthorhombic crystals are dark brown or black and opaque, and range in sp.gr. from 5·3 (columbite) to 7·3 (tantalite). It was in this mineral that C. Hatchett discovered, in 1802, the element columbium, so named because the specimen he examined came from America. Columbite is usually found as single crystals embedded in pegmatite or granite; for example, at Haddam and Middletown in Connecticut, Chesterfield in Massachusetts, brilliant crystals in granite at Standish in Maine, large masses up to 2000 lb. in granite veins in the Black Hills of South Dakota, and at several other American localities. At Ivigtut in Greenland it has been found in the cryolite deposit. Large crystals are found in the felspar quarries near Moss in Norway. Other localities are Rabenstein in Bavaria, Bushman Land in South Africa, Madagascar, etc.

L. J. S.

COLUMBIUM, NIOBIUM (Sym. **Cb**, **Nb**). At. wt. **92·91**. The name columbium is used in current American literature, although the element is now known as niobium in Great Britain, France, and Germany. The first name is due to Hatchett, who in 1802 isolated a new " earth " (Nb_2O_5) from a mineral found in Connecticut. He called the mineral columbite and the element columbium. It was not until 1844 that Rose (Pogg. Ann. 1844, **63**, 307, 693) observed a wide variation in the density of many tantalites and columbites, and of the acids derived from them, and realised that they contained two closely related elements. It was Rose who introduced the name niobium for Hatchett's columbium. In all probability Hatchett's " earth " was a mixture of Nb_2O_5 and Ta_2O_5. The name niobium and the symbol **Nb** will be used throughout this article, in accordance with the nomenclature adopted in the First Report of the International Union of Chemistry, 1936.

Niobium is a member of a group of comparatively rare metals, including tantalum, tungsten, molybdenum, titanium, and uranium, commonly occurring together in minerals found in the oldest Plutonic rocks, and especially in and around intrusions which traverse pegmatites and other extremely coarse-grained granite rocks. Monazite. and other minerals containing metals of the cerium group, zircon, cryolite, and fluorspar, and minerals containing lithium, cæsium, and rubidium, are often associated with these minerals, and are probably intimately connected with their genesis.

Although a rare metal, niobium exists as the pentoxide in a considerable number of minerals, in some of which—such as *pyrochlore* and columbite—it may be regarded as the essential constituent, while in others, although practically always present, its proportion varies from a mere trace up to an amount which justifies its being considered as the principal oxide.

Niobium occurs in minerals only as the pentoxide, Nb_2O_5, in combination with a base, the niobium in a few minerals (such as *wöhlerite*) which contain silica being present as a silico-niobate and never as a silicate of niobium.

A list of the principal minerals containing niobium will be given in the article TANTALUM, with which metal niobium invariably occurs in nature. From the technical point of view the principal niobium minerals are those which consist essentially of niobates of iron, manganese and lime, zirconia and metals of the cerium group being also usually present in, or at least intimately associated with, such minerals as contain lime.

The mineral richest in niobium is pyrochlore, a niobate of lime containing titanium, cerium, and thorium, together with other alkaline earths and alkali bases and some fluorine. The most important mineral, however, is the niobate of iron and manganese known as *columbite* or *niobite* (*q.v.*), in which the Nb_2O_5 may even exceed 78%.

New deposits are constantly being discovered, and niobium, like many others of the rare metals for which a demand now exists, will doubtless be found to occur in much larger quantities than is now generally known. One property in Western Australia is at present being operated exclusively for the production of tantalite-niobite concentrates. Considerable amounts are also available as by-products from the preparation of the rare earths employed for incandescent mantles, from tin and wolfram ores, and from the heavy waste material obtained in the dressing of cryolite.

Metallic niobium may be prepared by passing a mixture of the vapour of the pentachloride and hydrogen through a red-hot tube (Roscoe) Moissan reduced the pentoxide by means of carbon in an electric furnace, but the resulting niobium contained 2·5–3·4% of carbon. Von Bolton introduced a method of manufacturing niobium for metal filament lamps in which the pentoxide was mixed with paraffin and formed into threads, which were heated *in vacuo* to a temperature of over 1,900° by passage of an electric current. The use of niobium in lamp manufacture has now been discontinued.

Larger quantities of niobium were produced by von Bolton by reducing the pentoxide with aluminium powder, and heating the product, which contained some 3% of aluminium and some unchanged oxide, in an electric arc in vacuum. This treatment sufficed to vaporise the impurities out of the niobium. The metal is also obtained by reduction of the fluoride K_2NbF_7 with hydrogen. The product is a black powder from which residual hydrogen may be expelled by shaping it into small cylinders and melting *in vacuo* in an electric furnace. Marden and Rich (U.S.P. 1728941, 1927) have described the reduction of Nb_2O_5 by calcium in presence of a small quantity of alkali metal and of calcium chloride. This operation is carried out in a sealed tube at 900–1,000°.

The electrolytic production of niobium from a mixture of niobium and tantalum pentoxides was described by Isgarischev and Prede (Z. Elektrochem. 1933, **39**, 283–288). The oxide mixture was fused with potassium pyrosulphate and the melt extracted first with water and then with 20% potassium hydroxide solution. Electrolysis of the alkali extract with the addition of from 1–1·5% of dextrin, with a platinum anode and a copper cathode, yielded a deposit of pure niobium. Alternatively, the melt was extracted with saturated ammonium oxalate solution, with the addition of a smaller amount of saturated oxalic acid solution, or with citric acid solution, and electrolysed at a temperature above 80°. Niobium was thus deposited quantitatively, and tantalum pentoxide could be recovered from the electrolyte by acidifying with sulphuric acid. Electrolysis in acid solutions was found to be satisfactory for the electro-analysis of niobium-tantalum mixtures. The niobium deposits were resistant to corrosion by mineral acids.

Peirce (J. Amer. Chem. Soc. 1931, **53**, 2810) found that niobium, but not tantalum, could be electro-deposited at 103° from a saturated sodium carbonate solution in which the ignited pentoxide had been dissolved. A copper cathode and a current density of 3 amps. per sq. dm. were employed. Balke (Ind. Eng. Chem. 1935, **27**, 1166) states that metallic niobium may be produced by minor variations of the electrolytic method used for tantalum. The fused double fluoride K_2NbF_7 is electrolysed, using a cast-iron pot as cathode and a rod of graphite as anode, and adding niobium pentoxide to the molten bath.

The separation of niobium from tantalum is a problem chiefly of importance in connection with the preparation of tantalum, and will be dealt with fully under TANTALUM. The general method of extraction consists in fusing the ore with an alkali or alkaline salt, extracting the mixture of niobates and tantalates with water, and boiling the solution to cause hydrolysis, with production of an insoluble mixture of niobic and tantalic acids. This mixture on ignition gives the pentoxides Nb_2O_5 and Ta_2O_5. The preparation entails the removal in turn of tin, antimony, iron, manganese and similar elements, and also of titanium.

The separation of niobium and tantalum is a matter of considerable difficulty, owing to the close similarity of these two elements. One of the commonest methods is that developed by Marignac in 1866, depending on the different solubilities of potassium niobium oxyfluoride, K_2NbOF_5,H_2O (1 part in 12–13 parts of water at 17°–21°), and potassium tantalum fluoride, K_2TaF_7 (1 part in 150–160 parts of water containing a little hydrofluoric acid, at the same temperature). These two compounds are not isomorphous and do not form mixed crystals or solid solutions. In carrying out the separation the mixture of niobic and tantalic acids is dissolved in concentrated hydrofluoric acid and the correct amount of potassium fluoride is added. On concentration, the potassium tantalum fluoride separates first and is filtered off. The filtrate is concentrated further with the addition of more hydrofluoric acid and potassium fluoride, and yields crystals of potassium niobium oxyfluoride mixed with potassium tantalum fluoride. These two salts are then separated by recrystallisation.

Numerous alternative methods of separation have been suggested and applied. Thus, for example, a solution of potassium hexa-tantalate and-niobate is formed by dissolving 1 part of a mixture of Ta_2O_5 and Nb_2O_5 in 6–8 parts of water with the addition of 3–4 parts of potassium hydroxide. From the resulting solution pure tantalic acid is precipitated at 15–30° by the action of carbon dioxide or a bicarbonate (U.S.P. 1908473, 1934). Another method utilises the solubility of niobium pentoxide, and the insolubility of tantalum pentoxide, in a mixture of equal volumes of selenium oxychloride and concentrated sulphuric acid (Lehner, J. Amer. Chem. Soc. 1921, **43**, 21; Merrill, *ibid.* 1921, **43**, 2378). Hydrolysis of the extract after dilution yields niobic acid. Ruff and Thomas (Z. anorg. Chem. 1926, **156**, 213) found that niobium pentoxide is converted to the pentachloride by heating at 200-225° with carbon tetrachloride, whereas tantalum pentoxide is unaffected. Unfortunately, the metals cannot be separated by this means, as niobium pentachloride reacts with tantalum pentoxide, forming niobium oxychloride and tantalum pentachloride, which are not readily separated.

Metallic niobium melts at 1,950° (von Bolton, Z. Elektrochem, 1907, **13**, **145**) A lower value (1,700°) is recorded by Guertler and von Pirani, (Z. Metallk. 1920, **12**, 67; Ann. Phys. 1915, [4], **48**, 1034). Its electrical resistance is 0·1870 ohm for a wire 1 m. long and of 1 mm. diameter (*see also* Balke, Ind. Eng. Chem. 1929, **21**, 1002). It is less malleable or ductile than tantalum, but the rolled metal has a hardness greater than that of wrought iron and may be welded at a red heat. Balke (Ind. Eng. Chem. 1929, **21**, 1002) states that in the annealed condition niobium is more ductile than tantalum. Many of the properties of niobium as known at present were determined with a sample of the metal prepared by von Bolton (l.c.) by reducing the oxide with aluminium. This author gave the density as 12·7, but more recent values range from 7·4 to 8·56.

The powdered metal oxidises rapidly when heated in air, some nitride being formed together with the oxide, but the rolled or cast metal is but little affected, as a protective coating of oxide rapidly forms. It is practically unaffected by any acid except hydrofluoric acid, or by solutions of the alkalis, but is rapidly attacked by fused alkalis or alkaline nitrates.

Metallic niobium combines with hydrogen at a high temperature, and according to von Bolton a *hydride*, NbH, is formed. Hagen and Sieverts (Z. anorg. Chem. 1930, **185**, 225) have since shown, however, that the amount of hydrogen taken up is a function of temperature and pressure, and the formation of a true compound is very doubtful. The compounds of niobium have not yet been applied commercially, but the pentoxide and the fluorides, especially the double fluoride K_2NbF_7, are of interest in connection with the preparation of the pure compounds or metal from minerals. Niobium in amounts up to about 2% inhibits intergranular deterioration when chromium-nickel steels of the stainless type are exposed to elevated temperatures and chemical corrosion. Tantalum gives similar results, but a larger proportion of it is required (Becket and Franks, Trans. A.I.M.E. 1934, **113**, 143). Addition of niobium to steels containing 4–6% of chromium and 0·1–0·2% of carbon is found to inhibit the air-hardening property of such steels. Niobium has a limited use in valve manufacture.

Alloys of niobium have hitherto received relatively little attention. Iron and niobium appear to alloy in all proportions, and ferro-niobium may be formed directly by reducing the mixed oxides. Aluminium-niobium alloys have been produced by the Goldschmidt process, and a brittle alloy of chromium and niobium is formed by fusing green chromium oxide and niobium together in the electric furnace (Goldschmidt and Vautin, J.S.C.I. 1898, **17**, 543; Moissan, Bull. Soc. chim. 1902, [iii], **27**, 431). Alloys of nickel and zirconium with niobium and tantalum have been prepared, and it is claimed that the alloy containing zirconium can be heated to whiteness in air without oxidation or vaporisation (Canada P. 209342, 214118, 1921; U.S.P. 1334089, 1920).

The removal of tin from $Fe-Nb-Ta$ alloys obtained in the reduction of niobite is carried out by fusion with sufficient silicon to convert the niobium and tantalum to the silicide $(Nb,Ta)_2Si$. The resulting brittle alloy is powdered and boiled with hydrochloric acid to extract the tin. The purified powder may be melted and blown to remove silicon, or may be used direcly for the treatment of stainless steels (B.P. 450857, 1935). Ferrosilicon-niobium alloys are produced from a mixture of niobite, silicon, lime, and silica by fusion in an electric furnace (B.P. 434400, 1935).

Compounds of Niobium.

Niobium monoxide, NbO, has been described by various authors, but its existence is somewhat doubtful. It is said to be produced by reducing K_2NbOF_5 with sodium in an iron crucible, or by reducing $NbOCl_3$ with magnesium, and is described as a black material. It burns to the pentoxide when heated in air, ignites in chlorine, forming $NbOCl_3$, and is soluble in hydrochloric acid with evolution of hydrogen.

Niobium sesquioxide, Nb_2O_3, is formed by reducing niobium pentoxide with magnesium powder, or by heating the pentoxide in a stream of hydrogen at 1,250°.

Niobium dioxide, NbO_2, a black powder, is also formed by heating the pentoxide in hydrogen, or with magnesium. It burns when heated to redness in the air.

Niobium pentoxide, Nb_2O_5, is a white infusible powder of sp.gr. 4·53–4·8, according to the method of preparation. It is formed by direct oxidation of niobium, or of its lower oxides, and also, in the hydrated condition (niobic acid) by the hydrolysis of pentavalent niobium salts. The molecular heat of formation from the elements is 441,330 g.-cals. After strong ignition niobium pentoxide is insoluble in all acids except hydrofluoric acid. It dissolves, however, in molten potassium hydrogen sulphate, or ammonium hydrogen sulphate, and in fused alkali hydroxides or carbonates, although it is insoluble in solutions of alkalis. The niobium pentoxide content of a mixture of Nb_2O_5 and Ta_2O_5 may be determined by reducing the Nb_2O_5 to Nb_2O_4 by means of hydrogen, and determining the increase in weight on ignition. Ta_2O_5 is not reduced by hydrogen.

Niobic acid.—This term is applied to the more or less hydrated pentoxide formed by the hydrolysis of compounds such as niobium pentachloride or oxychloride. A similar material is formed by the action of mineral acids on alkali niobates. The gel is completely dehydrated by heating to 300° (*cf.* Süe, Compt. rend. 1932, **194**, 1745). Freshly precipitated niobic acid gels are soluble in acids and also in sodium or potassium hydroxide solution.

Numerous niobates have been described, only those of the alkali metals being soluble in water. Sodium metaniobate, $NaNbO_3$, is obtained in the anhydrous form by fusion of niobium pentoxide with sodium carbonate and sodium fluoride. It crystallises with seven molecules of water of crystallisation. Jander and Frey (Z. anorg. Chem. 1931, **196**, 321) have obtained products such as BaO,Nb_2O_5 and $4BaO,Nb_2O_5$ by heating barium carbonate with niobium pentoxide to 400–500°. Many other niobates have been described (*see* "Text Book of Inorganic Chemistry," edited by J. Newton Friend, vol. VI, part III, pp. 156–166), but their compositions and constitutions are in some cases uncertain.

Perniobic acid, $HNbO_4,nH_2O$, is obtained as a yellow amorphous powder on decomposing potassium perniobate with dilute sulphuric acid and dialysing the product, or by the action of 30% hydrogen peroxide on niobic acid. It loses oxygen at 100°, and forms hydrogen peroxide on heating with dilute sulphuric acid. Perniobates of the alkali metals of the general formula M_3NbO_8 are formed by treating the corresponding niobate with hydrogen peroxide and a solution of the base, and adding alcohol. They are white powders stable in contact with air, and decomposed by water.

Niobium pentafluoride, NbF_5, forms colourless, strongly refractive, monoclinic prisms, d^{18} 3·293, m.p. 75·5°, b.p. 217–220°/760 mm., and is obtained by the action of fluorine on niobium, or by treating niobium pentachloride with anhydrous hydrogen fluoride in a freezing mixture, and purifying by redistillation (Ruff and Zedner, Ber. 1909, **42**, 493; Ruff and Schiller, Z. anorg. Chem. 1911, **72**, 329). It is hygroscopic and is readily soluble in water, the solution yielding niobic acid on addition of ammonia or sodium hydroxide. It has a strong tendency to form stable double fluorides with the fluorides of other metals.

Niobium oxyfluoride, $NbOF_3$, is obtained by the action of hydrogen chloride on a fused mixture of niobium pentoxide and calcium fluoride at a red heat. It forms double salts with other metallic fluorides (*e.g.* Na_3NbOF_6, $(NH_4)_2NbOF_5$, $ZnNbOF_5,6H_2O$).

Niobium trichloride, $NbCl_3$, is a non-volatile, non-deliquescent, crystalline substance resembling iodine, and is formed by leading the vapour of the pentachloride through a heated tube. It forms long dichroic needles, which are oxidised on exposure to air and which yield niobium oxychloride, $NbOCl_3$, and carbon monoxide when heated in carbon dioxide (Roscoe, Chem. News, 1878, **37**, 26).

Niobium pentachloride, $NbCl_5$, is formed as yellow needles by heating niobium pentoxide mixed with charcoal in a stream of chlorine. It is also formed by heating the pentoxide with sulphur monochloride in a sealed tube at 200°, and fractionally distilling the products in a current of chlorine. It is produced, together with the oxychloride, by heating the pentoxide with carbon tetrachloride. It has m.p. 194°, b.p. 240·5°, sp.gr. 2·73–2·77, and gives a normal vapour density. It is soluble in carbon tetrachloride, chloroform and alcohol. On heating with 3% sodium amalgam in absence of air and extracting with water, *chloroniobium chloride*, $(Nb_6Cl_{12})Cl_2,7H_2O$, is obtained as black shining crystals, forming an olive green powder, insoluble in cold water, but soluble in hot water to an olive green solution. Only two of the chlorine atoms are ionic. When treated with the equivalent amount of sodium hydroxide, *chloroniobium hydroxide*,

$$(Nb_6Cl_{12})(OH)_2,8H_2O,$$

is formed as a black microcrystalline precipitate, and from this the *bromide*,

$$(Nb_6Cl_{12})Br_2,7H_2O,$$

is obtained. The hydroxide is soluble in excess of sodium hydroxide, and from the solution excess of concentrated hydrochloric acid precipitates a brown powder, $Nb_6Cl_{14},9H_2O$ (Harned, J. Amer. Chem. Soc. 1913, **35**, 1078).

Reduction of a solution of niobium pentachloride at a platinum cathode gives a blue solution, which is of a colloidal character; with gold chloride it gives a magnificent purple liquid, from which, on boiling, a purple precipitate deposits. This precipitate is similar to purple of Cassius; it colours glass a violet-red. According to Kiehl and Hart the blue solution contains tervalent niobium (*ibid.* 1928, **50**, 1608).

Niobium pentachloride forms an addition compound with piperidine, $NbCl_5,6C_5H_{11}N$, and gives similar compounds with related organic bases. It reacts with boiling benzene to give the compounds $3NbCl_5,C_6H_6$, $2NbCl_5,C_6H_6$, and $NbCl_5,C_6H_6$, and with naphthalene to give $NbCl_4(C_{10}H_7)$ and $NbCl_3(C_{10}H_7)_2$. With phenol in carbon disulphide solution the compound

$$Nb(OC_6H_5)_4Cl,$$

m.p. 233–235°, is formed (Funk and Niederländer, Ber. 1928, **61**, [B], 249, 1385). Niobium pentachloride reacts with glacial acetic acid to form the compound $Nb_2O_3Cl(OAc)_3$ (Funk and Niederländer, Ber. 1929, **62**, [B], 1688).

Niobium oxychloride, $NbOCl_3$, is prepared by the action of chlorine on a mixture of niobium pentoxide and carbon, and forms white silky crystals which can be sublimed.

Niobium oxybromide, $NbOBr_3$, and **pentabromide,** $NbBr_5$, also exist, but the formation of an iodide appears to be doubtful (*cf.* Barr, J. Amer. Chem. Soc. 1908, **30**, 1668).

Niobium nitride, NbN, is prepared by heating the pentoxide mixed with the calculated weight of carbon in nitrogen at 1,250°. It is a light grey powder, m.p. 2,050°, which is decomposed by alkali hydroxide (Friederich and Sittig, Z. anorg. Chem. 1925, **143**, 293–320). *Triniobium pentanitride,* Nb_3N_5, is prepared by prolonged heating of powdered niobium in nitrogen at 1,000°.

Niobium carbide, NbC, has been produced by heating niobium sesquioxide mixed with carbon in hydrogen at 1,200°. The molten metal also absorbs graphite to yield carbides of unknown composition. They are brittle and hard, and will scratch glass or quartz (Moissan, Bull. Soc. chim. 1902, [iii], **27**, 431). The use of a niobium carbide and a binder in a metal composition has been described (B.P. 391933, 1933).

Niobium boride, NbB_2, is formed as a hard, grey, crystalline material in the electrolysis of fused mixtures of alkali and alkaline earth borates and fluorides with niobic oxide. Any amorphous boron or calcium boride is removed from the product with dilute nitric acid. The crystals resist nitric and hydrochloric acids and aqua regia, but are easily oxidised and are slowly attacked by fused alkalis, and by cold hydrofluoric or sulphuric acid (Andrieux, Compt. rend. 1929, **189**, 1279).

Niobium phosphide, NbP, is formed by heating red phosphorus with metallic niobium at 550° (Heinerth and Biltz, Z. anorg. Chem. 1931, **198**, 168). It burns readily when heated in air. *Niobium arsenide* $NbAs_{1\cdot 8}$, is prepared by prolonged heating of the elements at 600°.

Niobium sulphide, NbS_2, has been prepared as a black powder by heating the elements together. Metallic niobium is not attacked by hydrogen sulphide. A second sulphide, Nb_2S_5, has been reported as formed by the action of H_2S and CS_2 on Nb_2O_5 at 1,000° (Hönigschmid, *ibid.* 1934, **219**, 161). *Niobium oxysulphide,* $NbOS_3$, is also formed as a black crystalline powder by heating the pentoxide in the vapour of carbon disulphide mixed with carbon dioxide.

For methods of analysing niobites and tantalites, and of detecting and estimating niobium, *see* CHEMICAL ANALYSIS (Vol. II, p. 602).

The *Arc Spectrum of Niobium* has been studied by Hildebrand (J. Amer. Chem. Soc. 1908, **30**, 1672); Barr (*ibid.* 1668), Mott (Trans. Amer. Electrochem. Soc. 1917, **31**, 372), and Laporte (Z. Physik, 1926, **39**, 128). The most persistent lines (" raes ultimes ") are given by de Gramont as λ4058·97 and λ4079·73Å (Compt. rend. 1920, **171**, 1106).

H. J. E.

COLZA OIL *syn.* for RAPE OIL.

COMFREY, *Symphytum officinale.* The common comfrey (Fam. Boraginaceæ), a riverside plant, has been used since Saxon times as an external application for wounds. The air-dry root contains 0·6 to 0·8% *allantoin* to which its healing action has been ascribed.

COMPRAL. A combination of amidopyrine and trichlorethylurethane (*Baeyer Products, London*). B.P.C.

CONARACHIN *v.* ARACHIN.

CONCHAIRAMIDINE *v.* CINCHONA ALKALOIDS (this vol., p. 160*a*).

CONCHAIRAMINE *v.* CINCHONA ALKALOIDS (this vol., p. 160*b*).

CONCRETE *v.* BUILDING MATERIALS.

CONCUSCONINE *v.* CINCHONA ALKALOIDS (this vol., p. 160*c*).

CONDENSERS. In order to convert the vapour of a substance into a liquid, it is necessary to remove a quantity of heat equal to the heat of vaporisation. The apparatus which effects this transfer of heat is called a *condenser.*

The shapes and forms of condensers are many and varied, but there are two distinct types under which almost all patterns can be classified. The two types are:

1. *Surface condensers,* in which the cooling medium is kept separate from the vapour to be condensed, and
2. *Jet condensers,* in which the cooling medium is supplied directly to the vapour either in the form of a spray or as a thin film.

It is apparent that the history and development of condensers are parallel to those of distillation methods. It was not until the practice of distillation was improved by the alchemists that methods of condensation received attention. The origins of alchemy can be traced back in the researches of Hoefer, " Histoire de la Chimie," 2nd ed., Paris, 1866; Kopp, " Geschichte der Chemie," Braunschweig, 1847; and Berthelot, " Les Origines de l'Alchimie," Paris, 1885; " Introduction à l'Étude de la Chimie des Anciens et du Moyen Age," Paris, 1887; " Collection des Anciens Alchimistes Grecs," Paris, 1887; and " Histoire des Sciences—La Chimie au Moyen Age," Paris, 1893. One of the earliest applications of condensation was in the preparation of mercury. The preparation of this element is described by Dioscorides. Cinnabar was heated in an iron pot and the vapours condensed in an earthenware cover, which was denoted by the Greek word "ambix." The Arabic prefix "al" was added, making the work "alambic," or, as it is known to-day, "alembic."

Pliny describes a primitive method which was used for obtaining turpentine from rosin. Fleeces of wool were hung over kettles, the vaporised oil condensing on the fibres of the wool. Sponges were used by sailors to obtain fresh water at sea. Alexander of Aphrodisias (third century), in his commentaries on Aristotle's "Meteorologica," states that, "They boil the sea water and suspend large sponges from the mouth of a brazen vessel to imbibe what is evaporated and, in drawing this off from the sponges, they find it to be sweet water."

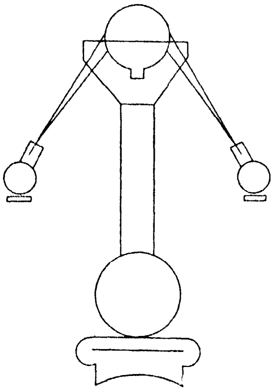


FIG. 1.

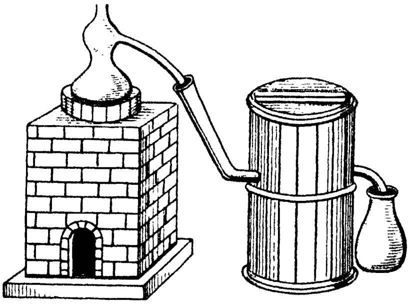


FIG. 2.

The earliest sketches of apparatus date from the time of the Greek alchemists of Alexandria. Zosimus, about the end of the third century, compiled a kind of chemical encyclopædia incorporating the work of previous writers. One of them was a woman alchemist by the name of Cleopatra who lived about the beginning of the Christian era. Cleopatra had written a treatise on gold-making which was called the "Chrysopœa." The "Chrysopœa" contains an illustration of an alembic to which two receivers are attached (Fig. 1).

It is probable that air cooling alone was used for the straight tube and alembic condensers up to the discovery of alcohol in Italy some time during the eleventh century. The use of water for cooling purposes was first mentioned by Raymond Lully (1235–1315) in his extensive writings on the curative and elixir properties of alcohol. Authentic drawings of apparatus of that period have not been found.

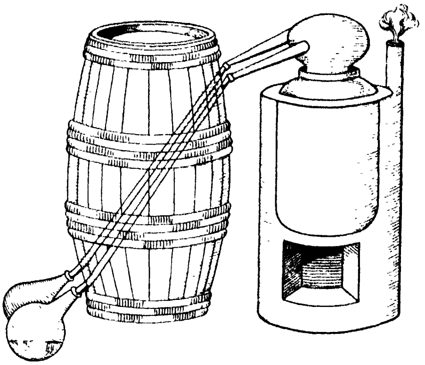


FIG. 3.

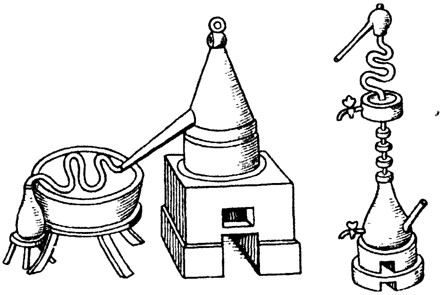


FIG. 4.

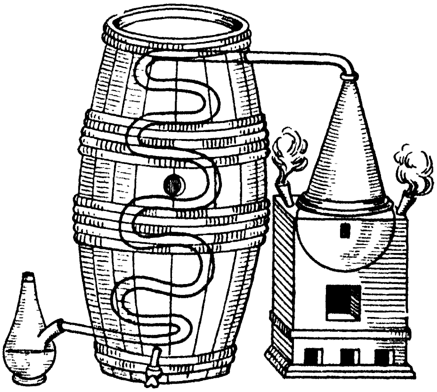


FIG. 5.

During the sixteenth century changes in the simple alembic condenser design were made to achieve better cooling. The first step was to lengthen the delivery tube which was then cooled by passing it through a tub of water. Fig. 2 is from " Thesaurus Euonymi Philiatri." The next improvement was to pass the tube diagonally through the water barrel to increase the cooling area, as in Fig. 3. The earliest illustration of a coil or worm condenser is shown in a work by Biringuccio (1540), Fig. 4.

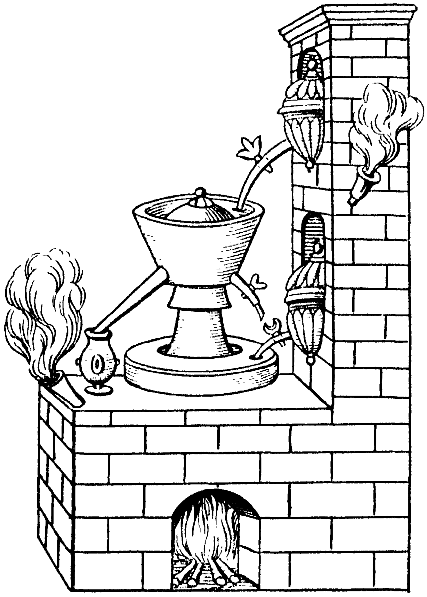


Fig. 6.

A similar design is shown in Fig. 5 which is taken from Lonicer (1551).

The first attempt at continuous cooling was tried some time in the middle of the eleventh century. Fig. 6 is taken from the French edition of Matthiolus's commentaries on Dioscorides (1501–1557).

During the eighteenth century there was no substantial advance made in condenser design. The worm cooler and the water-cooled alembic were in general use and were adequate for the uses to which they were put. The counter-current principle became better known and more widely used during the later part of the nineteenth century. Ettling ("Handwörterbuch der Reinen und Angewandten Chemie," 1842, Bd. 2, p. 531) assumed that Liebig deserved credit for the invention of the counter-current condenser, and to this day the simple straight-tube condenser is called a *Liebig condenser* (Fig. 9A). Kahlbaum (Ber. 1896, **29**, 69) claimed that Weiler was the first to see the advantage of admitting the cooling water at the end of the condenser furthest from the hot vapours. However, Speter (Chem.-Ztg. 1908, **32**, 3; Chem. Weekblad, 1931, **28**, 381–382) showed that the principle was first proposed by an unknown French chemist and later developed independently by Weiler and Gadolin. The condenser designed by Gadolin is shown in Fig. 7 (1778). Further investigation by Speter (Chem.-Ztg. 1908, **32**, 654) proved Lavoisier to be the author of the anonymous publication cited. Schelenz (Z. angew. Chem. 1910, **23**, 1978; Chem.-Ztg. 1909, **33**, 141, 154) believes this discovery was made by the French chemist Dariot (1533–1594), but was never appreciated until a later date. Poissonier (1770) also had realised the necessity of providing a large cooling surface and a counter-current flow of cooling water (Fig. 8).

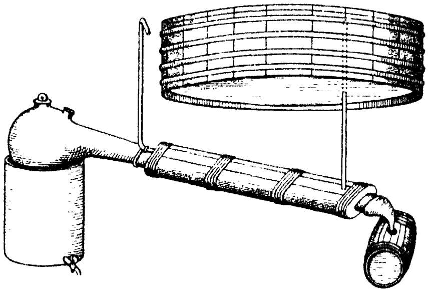


Fig. 7.

The surface condensers designed since this period do not differ fundamentally in principle from the ones just described, although the

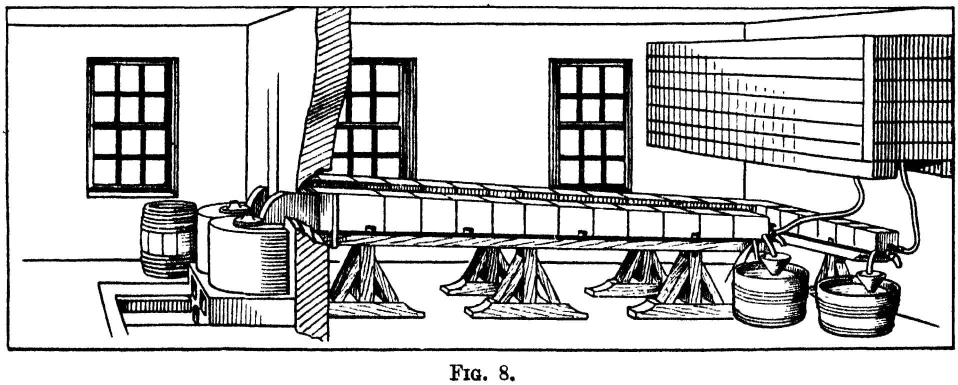


Fig. 8.

differences in detail are vitally important. The straight condensing tube has been replaced by spirals, bulbs, series of bulbs (Fig. 9D), combinations of these and divers methods of contacting the vapour and the cooling surface over a large area in a minimum of space. A special type of apparatus known as "reflux" condensers was designed to return condensed vapour back to a vessel containing boiling liquid without any sensible loss of vapour through evaporation. Reflux condensers are extensively used in extraction processes and in organic reactions where the loss of volatile solvent is to be prevented. The historical developments of the return condenser have been outlined by H. Meyer (Chem.-Ztg. 1910, **34**, 351, 421), L. Galates (*ibid.* 809), and Schelenz (Z. angew. Chem. 1910, **23**, 1975–1980).

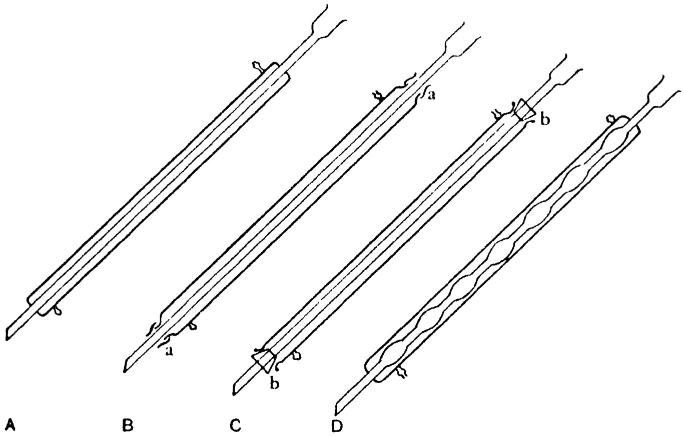


Fig. 9.

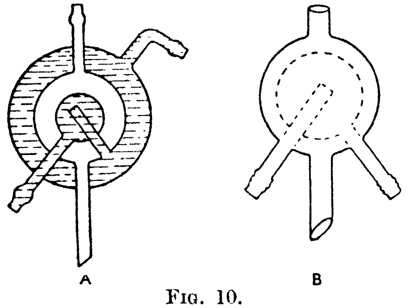


Fig. 10.

The simplest type of laboratory condenser that is widely used is the Liebig form shown in Fig. 9A. It consists of a straight cylindrical glass tube in which the vapour is condensed. The upper end is widened out slightly to facilitate connection with the still, and its lower end is cut off obliquely; a cylindrical glass jacket covers the greater portion of the length of the tube and, through it, by appropriate entrance and exit tubes, cold water is circulated in an upward direction. The glass jacket and inner tube may be fused together (9A), or connected by rubber (9B and C). For liquids of moderately high boiling-point (100°C. to 200°C.), it usually suffices to employ the inner tube merely as an air condenser. A form of condenser for use with high boiling-point liquids has been described by McCrea (J. Chem. Educ. 1930, **7**, 2963–2965).

With a view to exposing a large cooling surface, the portion of the condenser within the cooling jacket is sometimes made of approximately rectangular section. A condenser with expanded sections along the inner tube was described by W. Friese (Pharm. Zentr. 1913, **54**, 670). The apparatus consisted of an ordinary Liebig jacket inside which was a series of circular chambers with conical tops and bottoms, giving a large cooling surface. A condenser for accomplishing the same result is shown in Fig. 9D. The Soxhlet single bulb condenser which is commonly used as reflux condenser is shown in Fig. 10B. An all glass spiral pattern is shown in Fig. 11.

A slightly modified form of Liebig condenser is described by West (Ind. Eng. Chem. 1928, **20**, 737). The space between the inner and outer tubes is reduced to 1–1·5 mm. and the tubes are sealed together at the ends. The water consequently passes much more rapidly through the outer jacket and the cooling is found to be more effective (Fig. 12). The apparatus was the inner tube (West, Ind. Eng. Chem. [Anal.], 1930, **2**, 199).

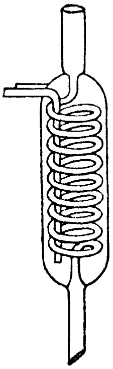


Fig. 11.

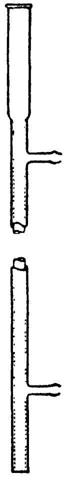


Fig. 12.

The first double-surface condenser was an air-water-cooled one. It was suggested by Hopkins (J.S.C.I. 1897, **16**, 979) that if the relative positions of the vapour and cooling stream of water are reversed, a larger area will be exposed. In Fig. 13A the water flows in the direction of the arrows. The outer jacket serves as an air-cooler, while the inner tube is water-cooled. Two forms of large-capacity laboratory condensers are described by Othmer (Ind. Eng. Chem. [Anal.], 1929, **1**, 153) in one of which the cooling is internal by means of a double-coiled tube, with water flowing through both tubes in parallel, thereby giving a maximum amount of cooling surface in minimum space (Fig. 13B). In the second type the cooling is external and there is a double-coiled inner tube for the vapour (Fig. 13C). Bajda (Ind. Eng. Chem. 1919, **11**, 52; the same in U.S.P. 1317262, 1919) passes the vapour through a preliminary air-cooler before passing it through the water chamber.

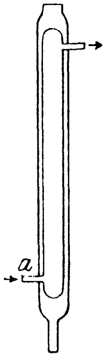


Fig. 13A.

A number of condensers of the "double-surface" type have been described. The vapours are condensed in the annular space between two surfaces, both of which are water-cooled, the design being such that one stream of water flows in succession over each. These condensers can be made quite short; they are readily fixed in a vertical position and occupy little bench space. A modified Soxhlet's ball type is shown in Fig. 10A. Several vertical condensers have been described by Friedrichs in which one of the two surfaces between which the vapours condense is constructed spirally (Z. angew. Chem. 1910, **23**, 2425–2426; 1912, **25**, 2200–2209). In certain extraction operations it is desirable to remove the solvent from the solvent-extract mixture without changing the apparatus. Bloom (Ind. Eng. Chem. 1910, **2**, 103) made such an apparatus (Fig. 14). And more recently Zinzadzé (Chem. Fabr. 1930, 113) has designed a double-chambered condenser for extraction or distillation. The top division is cooled by a coiled water tube and the liquid collects in the bottom of this division and may be withdrawn by a side tube, provided with a three-way tap, or returned to the lower division. Various modifications are described in the article (*see also* Zinzadzé, Biochem. Z. 1930, **220**, 177–184, 185–191; Bull. Soc. chim. 1931, [iv], **49**, 1204–1205).

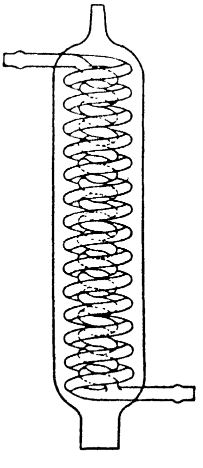


Fig. 13B.

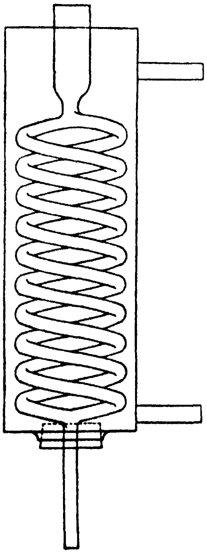


Fig. 13C.

The first comparison of the relative efficiencies of laboratory condensers was made by Dover and Marden (Ind. Eng. Chem. 1916, **8**, 834–836). The authors reported their conclusions as follows: "The rate of boiling has a very marked influence upon the efficiency of the condenser. The bore of the condenser has influence upon the efficiency of the condenser as has also a narrowing at the tip or a constriction anywhere in the tube. (Noticed in the spiral type where the spiral is fused on to the inner tube.) These conditions tend to cause chocking, and when this occurs loss is always disproportionately great. The length of the condenser is a factor in its efficiency (especially in the case of the Liebig form) for low boiling-point liquids. In the case of other forms, the length of the jacket has less influence than seems to be commonly supposed. In experiments where a long condenser can conveniently be used, the Liebig seems to be preferred because it is a much less costly condenser and can be easily cleaned. Where a short condenser is required, the Friedrichs seems best. The short Liebig or Allihn can be used to advantage only when the rate of condensation is not greater than from 2 to 3 drops per second, or when some means is used, such as a glass wool plug in the top of the condenser or a test-tube inverted over the top of the condenser, to prevent too rapid carrying away of the vapour by air currents."

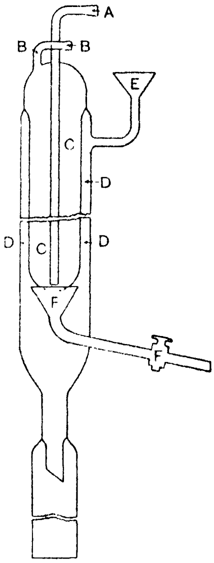


Fig. 14.

F. Friedrichs (Z. Angew. Chem. 1920, **33**, 29–32) presented a critical discussion of the various forms of laboratory condensers which had been described in the literature from the time of Liebig onwards. The screw-shaped condensing tube with five "threads" and provided with internal cooling jacket was most efficient. This form is more suitable for use as a reflux apparatus than is the spiral form. Mach and Herrmann (Chem. Fabr. 1931, **4**, 157, 170) tested condensers by using them as reflux apparatus; the loss of ether vapour under similar conditions was measured for each type. Results are tabulated for experiments with nine types of coolers. The best three coolers in the order of efficiency were: Liebig with four internal tubes, those with bulbs blown in the internal tube, and those with small jacket diameter. Counter-current cooling did not increase the efficiency. J. Friedrichs and H. von Kruska (Chem. Fabr. 1934, **7**, 284–287) made tests on ten types of apparatus. The results are tabulated and discussed. The West apparatus (Ind. Eng. Chem. [Anal.], 1930, **2**, 199) gave best results. E. J. Williams (School Sci. Rev. 1934, **16**, 271) recommends double-surface condensers for student and general laboratory use.

For condensing vapours in high vacuum work a highly specialised type of "trap" condenser is used. The vapour trap generally consists of a U-tube immersed in a refrigerant contained in a Dewar vessel (Fig. 15A). A useful design, believed to have been originated by S. Dushman, is shown in Fig. 15B, in which the vessel is unsilvered (*see* Hickman, J. Franklin Inst. 1932, **213**, 119–154. The refrigerant (usually solid CO_2 or liquid air) is placed in *a*, where it is insulated from the surroundings by the operating vacuum. The vacuum line connects at *b* and *c*. This type of trap presents a large condensing surface and imposes little resistance to gas flow.

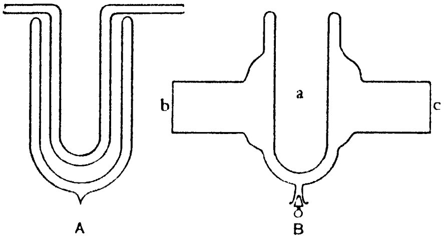


Fig. 15.

The condensers so far described are usually constructed of glass, but occasionally metals are employed. The use of aluminium for the inner tube of a Liebig condenser has been advocated by Norton (J. Amer. Chem. Soc. 1897, **19**, 153). A tube of block tin connected to a bulb of spun copper was used by Wiley (Ind. Eng. Chem. 1913, **5**, 151). Many agricultural chemists, who have to deal with numerous ammonia distillations, prefer a block-tin condenser. A convenient method of constructing a number of such condensers in series to be cooled by one stream of water is described by Barnard and Bishop (J. Amer. Chem. Soc. 1906, **28**, 999).

A useful metallic condenser is the ball type, shown in Fig. 10B, used on the reflux principle in numerous experiments involving extractions with volatile solvents. Storch's metallic reflux condenser is depicted and described in J.S.C.I. 1897, **16**, 979.

The spiral (worm) type of condenser is frequently constructed of metal (copper) and enclosed in a metal tank which can be filled with cold water; these condensers find considerable use in small plant for preparing distilled water. For this later purpose, a novel form of condenser is described in B.P. 6916/1905, which combines efficiency with extreme simplicity of construction. Special apparatus, devised for preparing pure distilled water (so-called conductivity water) on a laboratory scale are described by Bousfield (J.C.S. 1905, **87**, 740), Golding (J.S.C.I. 1906, **25**, 678), and by Hartley, Campbell, and Poole (J.C.S. 1908, **93**, 428). The use of silica tubes for such condensers is now more common.

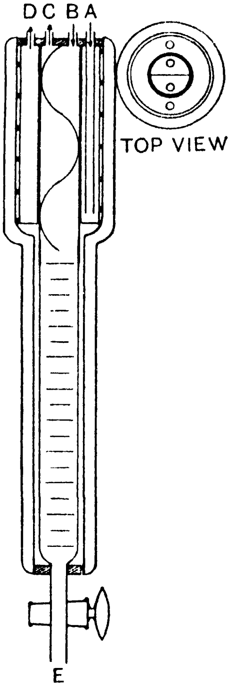


Fig. 16.

A condenser system made of glass and metal suitable for small analytical fractionating columns has been designed by Means and Newman (Ind. Eng. Chem. [Anal.], 1936, **8**, 231). It greatly resembles the top of a Prodbielniak column (*ibid.* 1931, **3**, 177). An evacuated glass jacket, silvered for efficient heat insulation, surrounds the burette and condenser. The condenser itself is a metal cylinder fitting into the top of the glass jacket and is insulated from the glass by means of an asbestos cord. The cooling medium is run down into the condenser through tube A (Fig. 16), and escapes at D. Compressed carbon dioxide or liquid air can be used, according to the temperature desired. The inner or condensing tube is of metal and contains a spiral strip extending down to the burette and dividing the tube into two compartments. Thus the vapours coming in at B pass down one side of the tube, condense, and fall into the burette. Displaced air passes up the other side of the dividing strip and emerges at C, losing condensable vapours in transit. The metal condenser tube is connected to the glass burette by soldering to the platinised glass. This provides an air-tight seal between the metal and glass. The condenser is adapted to distillations under reduced pressure, the vacuum connection being made at C and liquid extracted at E by any of the conventional methods for extraction of liquids during vacuum distillations. Littleton and Bates (Trans. Amer. Inst. Chem. Eng. 1926, **17**, 95–106) have discussed the relative merits of Pyrex glass and metal condensers. The overall coefficient of heat transfer from cooling water to vapour is not of the same order of difference as would be expected from the great difference in heat conductivity. The authors point out that an important factor in heat transfer is the film on either side of the cooling tube, the film itself acting as an insulator. This film is present on both Pyrex and metal condensers. (The effect of films is discussed below.)

In the design of large-scale industrial surface condensers stress is placed on efficiency. They are fundamentally heat exchangers designed for a special purpose. To secure a high coefficient of heat transfer from the condensing vapour to the cooling medium, Walker, Lewis, and McAdams ("Principles of Chemical Engineering," 2nd ed., p. 398, McGraw-Hill, New York) state that the requirements are: ". . . rapid circulation of the cooling medium to reduce the effective thickness of the water film through which heat must flow by conduction, immediate removal of the condensed liquid, and as complete removal as possible of non-condensable gases to prevent the formation of an insulating film of relatively stationary gas." Distillations done in vacuum help to meet the last requirement. A typical industrial surface condenser is shown in Fig. 17.

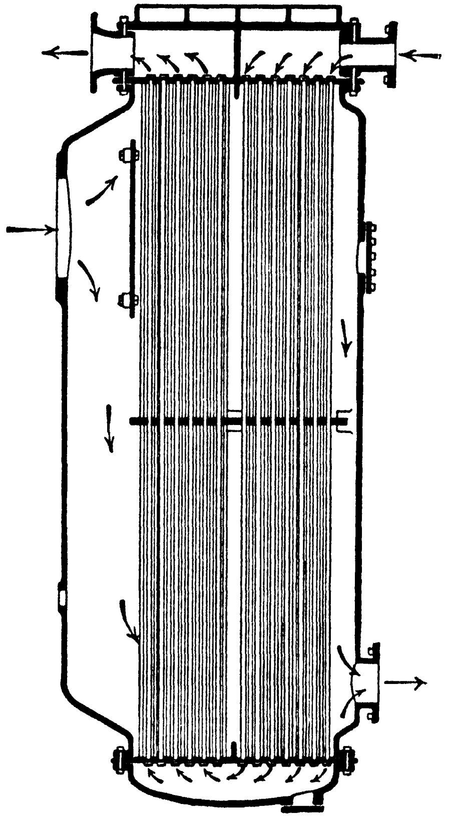


Fig. 17.

A surface condenser has the following advantages: the condensate is obtained uncontaminated with the cooling water, and in vacuum distillations it is not necessary to pump the water out of the system or remove it by means of a barometric draw-off.

A parallel jet condenser is shown in Fig. 18 and a fall-pipe jet-condenser in Fig. 19. Jet condensers have a large capacity per unit floor space, they are of simple construction, of low cost, and corrosive vapours may be condensed without destruction to the chambers. However, a large volume of cooling water is needed, and in vacuum operations the water must be removed from the system either by pumps or through a barometric column. Gases dissolved in the water are also liberated directly into the vacuum space and must be removed by the vacuum pumps.

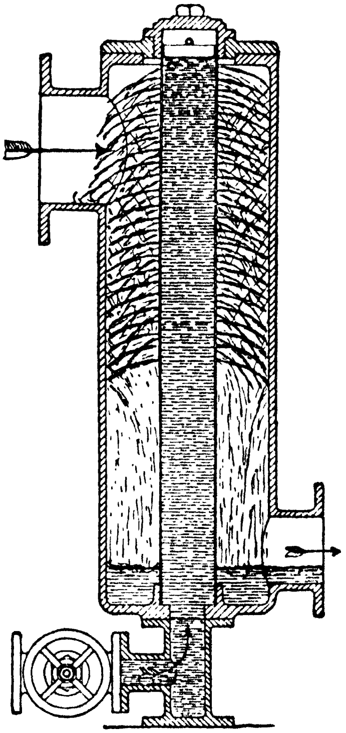


Fig. 18.

Industrial condensers of various kinds are described in the following: Hausbrand, "Evaporating, Condensing, and Cooling Apparatus" (trans. by Wright and rev. by Heastie), Benn, London; Sauvage, "Production et Condensation de la Vapeur," Baillière et Fils, Paris; Mironneau, "Technologie du Froid. T. I. Compresseurs et Condenseurs," Eyrolles, Paris; Low, "Condensers," McGraw-Hill, New York.

Other industrial condensers are described by the following: I.G. Farbenind. A.-G., "Apparatus for Condensing Vapours by Streams of Liquid Passed in the Same Direction," B.P. 301430, 1927; Kalindustrie A.-G., "Surface Condensers with Rotating Internal Cooling Drum," B.P. 306106, 1928; Leach, "Apparatus for Oil Refining and Condensing,” U.S.P. re-issues 19377–19378, 1935; Leach, “ Heat Exchange Apparatus Suitable for Condensing Oil Vapors,” U.S.P. 1980626 and 1980627, 1935; Gesellschaft für Linde’s Eismaschinen A.-G., “ Plant for Condensing Vapours from Gas Mixtures,” G.P. 604773, 1934; Cattanach, “ Heat Exchange Apparatus Suitable for Condensing Oil Vapors,” U.S.P. 1987051, 1935; Cameron, “ Condensing Hydrocarbon Vapors such as those of Gasoline,” U.S.P. 1992352, 1935; McDermet (to Elliot Company), “ Spray Device Suitable for Use with Condensers, Evaporators, etc.,” U.S.P. 2012454, 1935; Byer, “ Countercurrent Vapor Condenser,” U.S.P. 2013029, 1935.

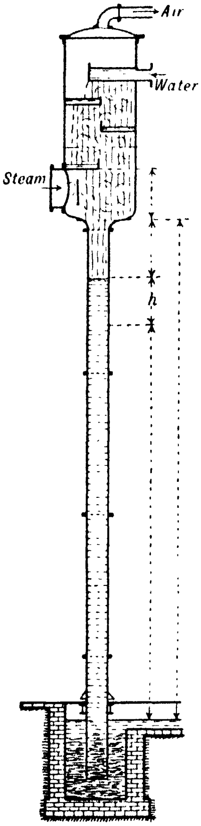


FIG. 19.

Some of the metals, such as zinc, lead, and cadmium, which are sufficiently volatile, are purified by evaporation and condensation. Several of the special types of apparatus for condensing metal vapours have been designed by: Fried. Krupp Grusonwerk A.-G., “Rotary Condenser for Metal Vapours,” F.P. 774132, 1935; Handwerk and Mahler (Assrs. to The New Jersey Zinc Company), “ Apparatus and Method for Condensing,” B.P. 421026, 1934; Fried. Krupp Grusonwerk A.-G., “ Apparatus for the Fractional Condensation of Metal Vapours,” B.P. 427233, 1935; G.P. 608800, 1935.

Many articles and many patents have been issued on the prevention of corrosion in metal condensers. Special alloys have been developed for use in making condenser tubes and jackets. The corrosion from the cooling water must be combatted as well as corrosion from the vapours. The preventive methods and the alloys have been discussed by: White, “ Corrosion Tests on Condenser Tubes,” Trans. Amer. Soc. Mech. Eng. (Fuels and Steam Power), 1931, **53**, No. 14, 247–251; Worthington, “ Copper-Nickel Tubes: Their Advantage for Steam Condensers,” Metal Progr. 1933, **24**, 20–24; Meurk, “ Protecting Surface Condenser Tubes from Corrosion,” U.S.P. 1978166, 1935; Korany and Bliss, “ Prevention of Corrosion in Gas Condensers,” Gas Age-Record, 1935, **75**, 33–34; Siegel, “ The Corrosion Resistance of Condenser Tubes as a Function of their Brinell Hardness,” Wärme, 1935, **58**, 173–177; Stager, “ Topochemical Viewpoints” (corrosion tests on brass condenser tubes are described), Korrosion u. Metallschutz, 1935, **11**, 73–88; Guillet, “ Condenser Tubes ” (the advantages of copper and brass for condenser tubes, especially where sea-water is used, are discussed), Cuivre et Laiton, 1935, **8**, 283–284; Whitney, “ Alloys that Resist Severe Corrosive Conditions,” Chem. Met. Eng. 1935, **42**, 370–371.

The foundation for the treatment as an exact science of condensers and condensation processes was laid by Mollier (Z. Ver. deut. Ing. 1897, Nos. 6 and 7). The first complete treatise was written by Hausbrand (1899), quoted above. Many articles and papers have followed since then. H. Braidy (Ind. Chim. 1919, **6**, 201–205, 234–237) presented a mathematical discussion of the theory of condensers and of cooling devices in general. Brewer and Stivers (Mech. Eng. 1921, **43**, 672–673) discussed the relative efficiencies of various types of cooling apparatus used as industrial units. Some features in condensing plant operation are given by Hardy (Proc. Univ. Durham. Phil. Soc. 1921, **6**, II, 66–83). The theory of fractional condensation was treated by Leslie (Oil News, 1924, **12**, No. 3, 15–16). Lewis (Amer. Gas J. 1928, **128**, No. 3, 42–44) has considered the cooling of non-condensible gases containing vapours which condense during the cooling process. Lewis discussed this case theoretically and showed that the heat of condensation is not transmitted through the gas film on the pipes and should not be considered in calculating the coefficients. The vapour passes through the film by diffusion and is condensed on the cold pipe surface (*see also* E. F. M. van der Held, Physica, 1934, **1**, 1153–1160, “ The Effect of Air on the Condensation of Water Vapour ”). Monrad and Badger (Ind. Eng. Chem. 1930, **22**, 1103–1112) brought to light several important papers on heat transfer, especially that of Nusselt (Z. Ver. deut. Ing. 1916, **60**, 541). When Nusselt’s equations for heat transfer in the condensation of saturated vapour on the outside of horizontal tubes were applied to the work of McAdams and Frost (Ind. Eng. Chem. 1922, **14**, 13–18), Morris and Whitman (*ibid.* 1928, **20**, 234–240), Clement and Garland (Univ. Ill. Eng. Expt. Sta. Bull. No. **40**, 1909), and Othmer (Ind. Eng. Chem. 1929, **21**, 576–583), the experimental results agreed fairly well with the calculated figures. When applied to data on vertical tubes (Badger, Monrad and Diamond, Amer. Inst. Chem. Eng. (Detroit meeting), 1930, 23 pp., preprint), the experimental results were several times higher than the theoretical. The authors attempted to explain this by calculating the point on a vertical tube where turbulence begins in the film of condensate. Nusselt assumed this film to be in viscous flow only. It was shown that turbulence begins a relatively short distance down the tube, and this may account for the high results as compared with Nusselt’s formula. A mathematical analysis similar to Nusselt’s, but assuming turbulence in the film, was not made. The variations in the degree of turbulence explain the great difficulty in making determinations of heat-transfer coefficients on vertical tubes.

A general review of heat-transfer processes which could be applied or are in actual operation has been given by Othmer (Ind. Eng. Chem. 1930, **22**, 988–993). The article notes such important developments as mercury and diphenyl heating, forced circulation evaporators, and high-pressure equipment (*see also* Badger, Monrad and Diamond, *l.c.*).

The effect of ribbed surfaces on the heat-transfer rates in condenser sections has been discussed by Olson and Wentworth (Oil and Gas J. 1923, **31**, Nos. 6, 14, and 16) and by Du Pont (Natl. Petroleum News, 1923, **24**, Nos. 46, 74–75, and 77–78).

Other papers on heat-transfer in condensers have been written by: Colburn and Hougen (Ind. Eng. Chem. 1934, **26**, 1178–1182; Chem. Age, 1935, **32**, 579–580); Heastie (Food, 1934, **4**, 110–112; 1935, **5**, 163–165); Frene (Refiner and Natural Gasoline Mfr. 1934, **13**, 390); Pavlov and Kravetz (Khim. Mashinostroenie, 1935, No. 4, 19–21); Du Pont (Natl. Petroleum News, 1935, **27**, No. 23, 110–111); Oldham (Ice and Cold Storage, 1934, **37**, 27–28).

In the realms of physical science, the word *condensation* has assumed a broader meaning, which includes the condensation on charged particles in the Wilson cloud chamber, the formation of fog, the vesicular state, and the adsorption on various types of surfaces, particularly capillary adsorption phenomena. These special processes are discussed under headings of adsorption and theories of adsorption (*v.* Adsorption).

Appendix.—Other forms of the Liebig condenser have been described: Ber. 1892, **24**, 3950; *ibid.* 1895, **28**, 2388; J.S.C.I. 1899, **18**, 707; Chem.-Ztg. 1902, **26**, 325; *ibid.* 1902, **26**, 633; *ibid.* 1904, **28**, 686; Bull. Soc. chim. 1904, [iii], **31**, 1116; Chem.-Ztg. 1904, **28**, 598; *ibid.* 1905, **29**, 809; B.P. 6916, 1905; Chem. Zentr. 1906, ii, 993; Editorial, L'industria chim. 1908, **8**, 184; Vigreux, Bull. Soc. chim. 1908, [iv], **3–4**, 855, 858; Chem.-Ztg. 1910, **34**, 116; Glaser, Aus. P. 1,943–II, 1911; Frankel, Biochem. Z. 1916, **74**, 165–166; Howden, Chem. News, 1918, **117**, 368; Gooderham, J.C.S. 1924, **125**, 2197; Beuschlein, Ind. Eng. Chem. [Anal.], 1929, **1**, 43–44; Naumann, Biochem. Z. 1930, **217**, 409–420; Crandall, J. Lab. Clin. Med. 1930, **16**, 89–91; Vaughn, J. Chem. Educ. 1931, **8**, 2433–2434; Hanak, J. Prakt. Chem. 1933, **136**, 202–204; Wagenseller, U.S.P. 1994934, 1935.

Other reflux condensers are described by: Chem.-Ztg. 1896, **20**, 462; Hahn, *ibid.* 1900, **24**, 619; Bull. Soc. chim. 1901, [iii], **25**, 476; Z. anal. Chem. 1901, **40**, 769; Chem.-Ztg. 1904, **28**, 598; Chem. Zentr. 1906, ii, 993; Chem. News, 1907, **95**, 52; Bull. Soc. chim. 1908, [iv], **3**, 855; Stoltzenberg, Z. angew. Chem. 1908, **21**, 2084; Merkel, *ibid.* 976; J.S.C.I. 1908, **27**, 962; Stolzenberg, Z. angew. Chem. 1909, **22**, 351; Vollrath, Chem.-Ztg. 1910, **34**, 1068; Anon., *ibid.* 716; Thorner, *ibid.* 1911, **35**, 597; Heide, *ibid.* 531; Fishburn, J. Amer. Chem. Soc. 1917, **39**, 1074; Vigreux, Bull. Soc. chim. 1917, [iii], **21**, 46–48; Vigreux, Ann. chim. anal. chim. appl. 1919, **1**, 211; Faust, Z. angew. Chem. 1919, **32**, I, 183–184; Shohl and Koch, Ind. Eng. Chem. 1921, **13**, 819–820; Mach and Lederle, Chem.-Ztg. 1921, **45**, 779.

Other double surface condensers are described by: J.S.C.I. 1905, **24**, 1190; Chem. Zentr. 1908, ii, 277; Kob, Chem.-Ztg. 1910, **34**, 116; Davies, *ibid.* 1911, **35**, 531.

J. C. H.

CONDURANGO. The dried bark of *Marsdenia Cundurango* Nichols (*Gonolobus Cundurango* Triana ; Fam. Asclepiadaceæ). It is obtained from a half-climbing or prostrate shrub of Ecuador.

Kubler (Arch. Pharm. 1908, **246**, 620) states that the principal constituents of the bark are dextrose, the glucoside *condurangin*, and a polyhydric alcohol *conduritol*. *Condurangin*, $C_{40}H_{60}O_{16}$, contains two methoxyl groups, is soluble in water, alcohol, and chloroform, insoluble in ether. Dilute sulphuric acid hydrolyses it to glucose and an amorphous powder, containing several substances ; alcoholic potash yields some cinnamic acid. *Conduritol*, $C_6H_{10}O_4$, crystallises from hot alcohol in colourless prisms, m.p. 142–143°, and yields a tetrabenzoyl derivative. According to Carrara (Gazzetta, 1891, **21**, i, 204 ; **22**, i, 236), commercial condurangin can be separated into two parts, one insoluble and the other soluble in water. The former is a white powder, $C_{20}H_{32}O_6$, m.p. 60–61° ; and the latter a yellow substance, $C_{18}H_{28}O_7$, m.p. 134°. Hager (Handbook, 1900) has further investigated these substances and named them *a*- and *b*-condurangin ; *a*-condurangin gives a green colour with Fröhde's reagent (conc. sulphuric acid and molybdic acid), *b*-condurangin does not. Carrara (*l.c.*) also isolated a yellow powder, $C_{30}H_{50}O_2$, which he named *conduransterin*, m.p. 52°.

CONDY'S FLUID. A solution of sodium permanganate, $NaMnO_4$, and sodium manganate, Na_2MnO_4.

CONESSIDINE, CONESSIMINE *v.* CONESSINE AND MINOR ALKALOIDS FROM HOLARRHENA SPP.

CONESSINE AND MINOR ALKALOIDS FROM HOLARRHENA SPP. *Holarrhena antidysenterica* Wall (Fam. Apocynaceae) or Kurchi-bark is well known in India as a remedy for dysentery as substitute for the more expensive ipecacuanha root. The plant contains about a dozen alkaloids which were partly isolated also from other *Holarrhena* spp., viz. *H. africana* D.C., *H. congolensis* S. Also *Wrightia zeylanica* contains similar alkaloids; it was from this plant that Haines first isolated conessine, also called *wrightine* in earlier papers (Trans. Med. Soc. Bombay, 1858).

A survey of early literature is given in a paper by Kanga, Ayyar and Simonsen (J.C.S. 1926, 2123). Early investigators mostly isolated conessine, which is the chief constituent of the Kurchi-bark ; to the recent work of Ghosh, Haworth, Bertho and Siddiqui we owe the knowledge of the minor Kurchi alkaloids.

According to Siddiqui and Pillay (J. Indian Chem. Soc. 1932, **9**, 553) the alkaloids in the bark are present as tannates and therefore difficult to extract with acidified EtOH or H_2O. On the same bark all hitherto known methods were tried and yields varying from 0·5 to 1·7% crude total alkaloids were obtained.

EXTRACTION (Siddiqui *et al.*, *l.c.*).—Dry powdered bark is percolated with a mixture of 80 parts of Et_2O and 10 parts $EtOH$, shaken with 10 parts of NH_4OH. The total alkaloids are precipitated by passing gaseous HCl through the percolate. The precipitate is dissolved in H_2O and sodium sulphate is added when a first fraction of "insoluble sulphates" is obtained (0·17% calculated for free base). The mother-liquor from the insoluble sulphates is made alkaline and exhausted with ether, when 2·1% "ether-soluble bases" are obtained. A fraction of this ether residue is soluble in light petroleum and is subsequently precipitated from the moist petroleum with CO_2, while a fraction remains in the solvent. The bases insoluble in light petroleum are fractionated from $CH_3 \cdot CO_2Et$ with CO_2. Finally three main fractions are obtained:

(*a*) Sulphates insoluble in H_2O.

(*b*) Carbonates insoluble in light petroleum.

(*c*) Bases soluble in light petroleum.

Fraction (*c*) (tertiary bases) gives 0·4–0·5% *conessine*; last traces of other alkaloids are removed by the "light petroleum-carbonate method." Conessine may be purified by re-crystallisation of its hydrogen-oxalate (Pyman, J.C.S. 1919, 163; Kanga, Ayyar and Simonsen, *l.c.*). From the mother liquors of the oxalate, the hydrobromides are prepared and the base fractionally precipitated from this salt, the middle fraction yields iso*conessimine*.

Fraction (*b*) contains secondary bases which are stronger than conessine. The bases were fractionally precipitated with ammonia, the first fraction containing "insoluble sulphates" and a fraction of "soluble sulphates." The third fraction contains some more conessine and chiefly "carbonates insoluble in light petroleum." The latter are united with the middle fraction and the hydriodides precipitated with KI (0·3%). After recrystallisation from $MeOH$ and $EtOH$ the carbonate is precipitated from light petroleum solution, the free base prepared and recrystallised from moist $CH_3 \cdot CO_2Et$, when pure conessimine (0·02%) is obtained. A later description (Siddiqui, J. Indian Chem. Soc. 1934, **11**, 284) recommends dissolving fraction (*b*) in moist $CH_3 \cdot CO_2Et$ and precipitating the more strongly basic di-secondary *conimine* as carbonate whilst *conessimine* and *iso*conessimine remain in solution and are separated from each other by means of fractional crystallisation from $CH_3 \cdot CO_2Et$ in which *iso*conessimine is more soluble than conessimine.

Fraction (*a*) is treated with 10% HCl, the white granular residue is dissolved in 10% alcoholic HCl and the sulphates precipitated from the hot neutralised solution with H_2SO_4. The recovered bases are recrystallised from $MeOH—CH_3 \cdot CO_2Et$, when *holarrhine* (0·02%) separates; from the concentrated mother-liquors *holarrhimine* is obtained.

Bertho, von Schuckmann and Schönberger (Ber. 1933, **66**, [B], 786) fractionated commercial mother-liquors of the fraction soluble in light petroleum (Siddiqui's fraction *c*) with conessine as chief constituent). By a process not given in detail they isolated three new alkaloids: *conessidine*, *conkurchine*, and *kurchenine* (yield of each alkaloid about 10% of conessine obtained).

Haworth (J.C.S. 1932, 631), by extracting the seeds of *H. antidysenterica*, obtained conessine and *norconessine*. The two bases were separated by the hydrogen-oxalate method.

Sudhamoy, Ghosh and N. N. Ghosh (J. Indian Chem. Soc. 1928, **5**, 477) extracted Kurchi-bark with $EtOH$. The total alkaloids (1·3%) were first precipitated with tartaric acid, when the tartrates of conessine and *kurchicine* separate, the two alkaloids are fractionated by recrystallisation of the sulphates and the free bases from $CHCl_3$ and light petroleum. The mother-liquors from the precipitated tartrates contain *kurchine*.

Peacock and Chowdhury (J.C.S. 1935, 734) exhausted Kurchi-bark with $EtOH$; from the crude alkaloids (1%) they obtained an insoluble hydrochloride-fraction which yielded a new alkaloid *lettocine* (0·1%).

HOLARRHENINE is an alkaloid extracted with very dilute HCl from the bark of *H. congolensis* (Pyman, *l.c.*); conessine (0·9%) was removed from the crude alkaloids by shaking out the alkaline solution with light petroleum. The alkaline mother-liquors were in turn extracted with Et_2O, when a small quantity of holarrhenine was obtained.

The separation of the holarrhena alkaloids is extremely difficult and it is not clear yet whether the number of bases can be reduced owing to the fact that several of those isolated are identical (*cf.* Siddiqui, *l.c.* and Bertho *et al.*, *l.c.*).

Conessine (I), $C_{24}H_{40}N_2$, $[\alpha]_D$ −1·9° (in $CHCl_3$) or +21·6° (in absolute $EtOH$), m.p. 126° crystallises from acetone in short needles or large prismatic plates, easily soluble in all organic solvents. (I) is a ditertiary base containing three NMe-groups; it is sensitive to light and atmospheric influences. $B \cdot 2HCl$ silky needles (from $MeOH$-acetone), $[\alpha]_D^{20}$ +9·32°, m.p. 338–340°; $B \cdot 2HI$ colourless bars, easily soluble in $MeOH$, less so in H_2O or $EtOH$; $B \cdot HgCl_2 + 2HCl$ needles, sparingly soluble also in hot H_2O; B·dimethiodide, slightly yellow octahedra, easily soluble in H_2O or $EtOH$, m.p. above 285°, it yields NMe_3 on distillation with $AgOH$.

Conessimine (II) (Siddiqui *et al.*, *l.c.*), $C_{23}H_{38}N_2$, $[\alpha]_D^{35}$ −22·25° (in $CHCl_3$), m.p. 100°, microscopic needles (from dry light petroleum, $CH_3 \cdot CO_2Et$ or acetone), or m.p. 91° (dihydrate), long slender needles (from moist $CH_3 \cdot CO_2Et$), b.p. 230°/1·8 mm. (II) contains two $N—Me$-groups and one active H-atom (Zerewitinoff). Mono - nitroso - compound, mono - benzoyl-(II), m.p. 121°, monoacetyl-(II) (oil). (II) yields (I) on methylation with $HCHO$ and $HCOOH$; (I) therefore is mono-methyl-(II). B·carbonate unstable; $B \cdot 2HCl$ amorphous, exceedingly soluble in H_2O and $EtOH$, $[\alpha]_D^{36}$ −15·1°, m.p. 342°; $B \cdot 2HI$, m.p. 318–319° (from H_2O); B·picrate, long rectangular plates (from $EtOH$) very sparingly soluble in hot H_2O.

Holarrhimine (III) (Siddiqui *et al.*, *l.c.*), $C_{21}H_{36}ON_2$, $[\alpha]_D^{25}$ −14·19°, m.p. 183°, crystallises from $CH_3{\cdot}CO_2Et$ in star-shaped radiating needles. (III) is very soluble in EtOH and $CHCl_3$, almost insoluble in Et_2O and light petroleum. Diacidic base, no OMe or NMe groups, three active H-atoms (Zerewitinoff). B·carbonate is unstable. B·2HCl, $[\alpha]_D^{25}$ −22·80°, m.p. 345°, broad plates, easily soluble in EtOH, less so in H_2O ; B·2HBr thin plates and broad needles, m.p. 358–360°, sparingly soluble in H_2O ; B·picrate yellow plates, m.p. 198–200° (anhydr.), fairly soluble in hot H_2O.

Holarrhine (IV) (Siddiqui, *et al.*, *l.c.*), $C_{20}H_{38}O_3N_2$, $[\alpha]_D^{25}$ −17·01°, m.p. 240°, crystallises from MeOH—$CH_3{\cdot}CO_2Et$ in needles, easily soluble in MeOH and EtOH, sparingly so in $CHCl_3$, almost insoluble in $CH_3{\cdot}CO_2Et$, Et_2O or light petroleum; (IV) appears to be a secondary base. B·picrate semi-crystalline powder, m.p. above 320°.

***iso*Conessimine** (Siddiqui *et al.*, *l.c.*) (V), $C_{23}H_{38}N_2$, $[\alpha]_D^{28}$ +30·0° (in absolute EtOH), m.p. 92°, crystallises from light petroleum or acetone in needles, from moist $CH_3{\cdot}CO_2Et$, as dihydrate, m.p. 88–92° ; (V) is readily soluble in all organic solvents, it contains two NMe-groups and one active H-atom (Zerewitinoff). (V) on methylation with HCHO and HCOOH yields (I), (I) therefore is monomethyl-(V); N-benzoyl-(V) m.p. 159–160° and N-acetyl-(V) m.p. 127–128° are monoacidic bases.

(V).carbonate is unstable, B·2HCl is crystalline, m.p. 335°, exceedingly soluble in H_2O or EtOH ; B·2HI needles, m.p. 316°, readily soluble in cold H_2O (difference from (I)) ; B·picrate, yellow rectangular plates and broad needles from dilute EtOH, m.p. 198–200° (anhydr.).

Conimine (Siddiqui, *et al.*, *l.c.*) (VI), $C_{22}H_{36}N_2$, $[\alpha]_D^{28}$ −30° (in absolute EtOH), m.p. 130°, crystallises from fairly concentrated solutions. Et_2O, light petroleum $CH_3{\cdot}CO_2Et$, or acetone in needles, from moist $CH_3{\cdot}CO_2Et$ as hydrate. (VI) contains two active H-atoms (Zerewitinoff) and one NMe-group. (VI) on methylation with HCHO and HCOOH yields (I) ; (I) is dimethyl-(VI), N, N-dibenzoyl-(VI) m.p. 250°, N, N-diacetyl-(VI) (m.p. 139–140°), N, N-dinitroso-(VI) m.p. 206–207°. B·2HCl needles, m.p. 318–320°, easily soluble in EtOH and H_2O ; B·2HI prismatic rods, m.p. 293°, fairly soluble in EtOH, less in H_2O ; B·picrate, brilliant yellow prismatic rods from H_2O, m.p. 140–141°, very sparingly soluble in hot EtOH and H_2O.

Conessidine (Bertho *et al.*, *l.c.*) (VII), $C_{21}H_{32}N_2$, $[\alpha]_D^{21}$ −52·2° (in $CHCl_3$), m.p. 123°, crystallises from acetone in thin needles or thick crystals. (VII) contains one NMe-group. B·2HI faintly yellow needles from H_2O, m.p. 259° ; B·$2HClO_4$ thin needles from H_2O, m.p. 243° (decomp.).

Conkurchine (Bertho *et al.*, *l.c.*) (VIII), $C_{20}H_{32}N_2$, $[\alpha]_D^{21}$ −67·4° (in EtOH), m.p. 153°, crystallises from Et_2O or EtOH—H_2O in small needles, easily soluble in $CHCl_3$, MeOH, EtOH, acetone, benzene, sparingly soluble in Et_2O or light petroleum. (VIII) does not contain NMe-groups. Methiodide amorphous; sulphate m.p. 342°, oxalate m.p. 325°, and acetyl-compound m.p. 233° are crystalline.

Kurchenine (Bertho *et al.*, *l.c.*) (IX), $C_{21}H_{32}O_2N_2$, $[\alpha]_D^{21}$ −92° (in 2N-HCl), m.p. 335–336°, crystallises from MeOH in thin leaflets, insoluble in Et_2O, sparingly soluble in MeOH and EtOH. (IX) does not contain OMe nor NMe-groups. B·sulphate crystalline, $[\alpha]_D$ −78·3° (in H_2O).

Norconessine (Haworth, *l.c.*) (X), $C_{23}H_{38}N_2$, $[\alpha]_D$ +6·7° (in absolute EtOH) is an oil b.p. 240/0·7 mm., very readily soluble in all organic solvents, it contains three NMe-groups. B·oxalate nodules, m.p. 225–227° from EtOH or H_2O ; B·2HCl slender needles from EtOH-acetone, m.p. 340° (decomp.) ; B·dimethiodide pale yellow prisms m.p. 310–312° (decomp.).

Kurchicine (Ghosh *et al.*, *l.c.*, and Ghosh and Bose, Arch. Pharm. 1932, **270**, 100), (XI) $C_{20}H_{36}ON_2$, $[\alpha]_D$ −11·4° (in $CHCl_3$), m.p. 175°. crystallises from $CHCl_3$-light petroleum in needles, easily soluble in EtOH and $CHCl_3$, sparingly soluble in benzene and acetone, insoluble in light petroleum. B·2HCl needles, easily soluble in H_2O, less so in EtOH, m.p. above 260° ; B·H_2SO_4,$2H_2O$ sparingly soluble in cold H_2O, leaflets, m.p. above 270°.

Kurchine (Ghosh *et al.*, *l.c.*) (XII), $C_{23}H_{38}N_2$, $[\alpha]_D^{32}$ −7·57° (in $CHCl_3$), m.p. 73–75°, b.p. 233°/1 mm., crystallises from Et_2O in needles, easily soluble in most organic solvents. B·2HCl,H_2O rhombic needles from H_2O, easily soluble in H_2O, less so in EtOH, decomp. about 220° ; B·2HBr needles from H_2O, easily soluble in H_2O and EtOH ; B·H_2SO_4 flat needles from H_2O, sparingly soluble in cold H_2O, decomp. at 270°.

Lettocine (Peacock and Chowdhury, *l.c.*) (XIII), $C_{17}H_{25}O_2N$, light-brown, microcrystalline powder (from $CHCl_3$-light petroleum), m.p. 350–352°, soluble in EtOH and $CHCl_3$, sparingly soluble in Et_2O and light petroleum; B·picrate, m.p. 198° (from absolute EtOH) ; B·methiodide, m.p. 235° (from hot MeOH). Does not yield an acetyl-compound.

Holarrhenine (Pyman, *l.c.*) (XIV), $C_{24}H_{38}ON_2$, $[\alpha]_D$ −7·51°, m.p. 197–198°, crystallises from $CH_3{\cdot}CO_2Et$ in silky needles and is readily soluble in EtOH and $CHCl_3$, sparingly so in cold $CH_3{\cdot}CO_2Et$, acetone, or Et_2O. B·2HBr flat needles (from H_2O), m.p. 265–268°. (XIV) contains three NMe-groups and yields an acetyl-compound which is still diacidic.

CONSTITUTION OF HOLARRHENA ALKALOIDS.—It has already been mentioned that (I) is obtained by introduction of one Me-group into (II) or (V) and of two Me-groups into (VI) (Siddiqui, *l.c.* 1934, 288, 290). By demethylation of (I) with BrCN (von Braun's method) (V) and (VI) are obtained (Siddiqui *et al.*, J. Indian Chem. Soc. 1934, **11**, 787). They conclude from their experiments that in (I) one N-atom is purely aliphatic forming the group $—NMe_2$; the second N-atom as $>NCH_3$ is a member of a heterocyclic ring-system.

(I) contains one double-bond and yields *dihydro-conessine* m.p. 105° on hydrogenation (Späth and Hromatka, Ber. 1930, **63,** 126 ; Osada, Amer. Chem. Abstr. 1928, **22,** 429) ; bromine is added (Ulrici, Arch. Pharm. 1918, **256,** 76) and with H_2SO_4 and KIO_3 (I) may be oxidised to *dioxy-conessine* m.p. 294–295° (Warnecke, Ber. 1886, **19,** 60 ; Ulrici, *l.c.*, 71 ; Giemsa and Halberkann, Arch. Pharm. 1918, **256,** 201). The Hofmann and Emde degradation of (I) was studied by Späth and Hromatka (*l.c.*, with information concerning earlier results). The first step of the degradation of (I)-dimethohydroxide removes the aliphatic N-atom, opens the heterocyclic ring, and yields apo*conessine*, m.p. 69° (*see* Kanga, Ayyar and Simonsen, *l.c.*). *Apo*Conessine is then degraded by Emde's method, when a nitrogen-free compound, $C_{21}H_{30}$, m.p. 74–76° is obtained. Oxidation experiments did not show any results; no benzene-ring seems to be present in (I). Späth and Hromatka conclude that (I) contains four reduced carbocyclic rings and a hetero-cyclic group with a side chain containing a double bond. The double bond may however be in the hetero-ring. No further details about the constitution of the Kurchi alkaloids are known.

PHYSIOLOGICAL ACTION OF KURCHI ALKALOIDS.—Bark and seeds of *Holarrhena antidysenterica* are used in India against dysentery. Acton and Chopra (Indian Med. Gaz. 1929, **64,** 207, quoted by Ghosh and Bose, *l.c.*) state that the total alkaloids of Kurchi-bark have an action like emetine, but they are less expensive and exert no blood-depressor action ; the iodo-bismuth compound of the total alkaloids is given orally (*cf. also* Brown, Brit. Med. J. 1922, I, 993). The physiological action of the bark and its extracts in the treatment of intestinal troubles may also be due to the fact that the tannates, as which the alkaloids occur, would remain undissolved in the acid juices of the stomach and pass on to the seat of the disease in the intestines (Siddiqui, *l.c.*). Pure conessine gives unexpectedly poor results; evidently some other alkaloid present in "conessine" is responsible for the antidysentery action.

Conessine does not influence bird-malaria (Goodson, Henry and Macfie, Biochem. J. 1930, **24,** 874), but even in very dilute solution it acts on tubercle bacilli (Meissner and Hesse, Arch. exp. Path. Pharm. 1930, **147,** 339).

For action of norconessine, *cf.* White (J. Pharm. Exp. Ther. 1933, **48,** 79) and of holarrhenine, *cf.* Burn (J. Pharmacol. 1915, **6,** 305, quoted by Pyman).

Schl.

CONGLUTIN. A globulin protein contained in the seeds of lupins.

CONHYDRINE one of the several poisonous alkaloids found in hemlock. *v.* CONIUM ALKALOIDS.

CONICEINE α-, β-, γ-, δ-, ϵ, and ψ- *v.* CONIUM ALKALOIDS.

CONIFERIN, $C_{16}H_{22}O_8,2Aq.$, m.p. 185°, $[\alpha]_D$ −67°, the β-glucoside of the fir tree, yields glucose and coniferyl alcohol when hydrolysed by emulsin. It has the formula :

$$C_6H_{11}O_5{\cdot}O{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}CH_2OH$$

On careful oxidation with chromic acid glucovanillin is formed which may be further oxidised to glucovanillic acid or reduced to glucovanillyl alcohol. All three glucosides are hydrolysed by emulsin. Coniferin at one time was used for the synthesis of vanillin.

It has been synthesised by Pauly and Feuerstein (Ber. 1927, **60,** [B], 1031) via glucoconiferylaldehyde, which can be reduced by the rather unusual method of adding it to a solution of sugar undergoing brisk fermentation.

It was discovered in the cambial sap of *Larix decidua* Mill., and occurs in the saps of the conifers in general ; it is found also in beetroot and asparagus.

It crystallises in colourless rosettes of pointed needles, sparingly soluble in cold water. The aqueous solution has a slightly bitter taste. When moistened with phenol and concentrated hydrochloric acid, an intense blue colour is formed ; it is soluble in concentrated sulphuric acid with a red coloration.

E. F. A.

CONIINE *v.* CONIUM ALKALOIDS.

CONIMINE *v.* CONESSINE AND MINOR ALKALOIDS FROM HOLARRHENA SPP.

CONIUM ALKALOIDS. Coniine is one of several poisonous alkaloids found in hemlock, *Conium maculatum* Linn. (Fam. Umbelliferæ) (0·2–0·9% in not quite ripe seeds). Hemlock (Fr. *Grande Ciguë* ; Ger. *Giftschierling*) is a tall biennial of the temperate regions of Europe, Asia and America and was the essential ingredient in the potion administered to condemned criminals by the Greeks. Besides *d*- and *l*-coniines, hemlock contains N-methyl-*d*- and *l*-coniine, γ-coniceine, conhydrine, and pseudoconhydrine. Power and Tutin (J. Amer. Chem. Soc. 1905, **27,** 1461) found a similar mixture of alkaloids in fool's parsley (*Æthusa Cynapium* Linn.).

EXTRACTION.—According to Chemnitius (J. pr. Chem. 1928, [ii], **118,** 25) coniine is prepared from finely ground seeds (0·4–0·5% total alkaloids) by mixing with wood wool, moistening with 15% aqueous NaOH, and extracting four times with warm Et_2O in a copper vessel. The concentrated extract is acidified with 50% acetic acid and Et_2O totally evaporated. After cooling, solidified fat is skimmed off, and the acid solutions are washed with Et_2O, excess of 35% NaOH is added, the alkaloids extracted with ether and finally fractionated in a current of hydrogen. The fraction boiling up to 165° is converted into coniine salts ; at 166–174° "coniinum purum" of commerce distils and the distillate above 174° is fractionated for *coniinum purum* and *conhydrine.* If the temperature is not raised above 185° conhydrine is left behind.

According to von Braun (Ber. 1905, **38,** 3108) if the fraction boiling up to 190° (containing no conhydrine) is benzoylated, the unchanged tertiary *N-methylconiines* can be removed from the ethereal solution by dilute acid. The ethereal solution is concentrated and poured into light petroleum when most of the benzoyl-δ-aminobutylpropylketone formed by interaction of benzoyl chloride with γ-*coniceine* is precipitated. The solvent is then distilled off and the residue fractionated when the benzoyl-*d*- and *l*-coniines distil at 200–210°/16 mm., and are thus separated from any residual derivative of γ-coniceine Benzoyl-δ-aminobutylpropylketone and the benzoyl-coniines can easily be converted into the parent alkaloids by hydrolysis.

Pseudoconhydrine usually accompanies conhydrine, from which it can be separated as **EtOH**-insoluble hydrochloride (Löffler, Ber. 1909, **42**, 116). For separation of coniine and pseudoconhydrine, *see* Späth, Kuffner and Ensfellner (Ber. 1933, **66**, [B], 591).

***d*-Coniine** (I), $C_8H_{17}N$, $[\alpha]_D^{19}$ +15·7°, m.p. −2°, b.p. 166–167°/760 mm., is a colourless, strongly alkaline liquid having a peculiar penetrating odour and a burning taste. (I) is slightly soluble in cold H_2O, less so in hot (turbidity on heating); it is steam-volatile and easily soluble in **EtOH**, readily soluble in Et_2O, sparingly so in $CHCl_3$. Exposed to the atmosphere (I) slowly darkens and resinifies. (I) dissolves in CS_2 forming a complex thiocarbamate (Melzer, Arch. Pharm. 1898, **236**, 701). $B \cdot HCl$, large rhombs (from H_2O), m.p. 220° ; $B \cdot HBr$ needles, m.p. 211° ; $B_2 \cdot H_2PtCl_6, H_2O$ orange-yellow crystals from H_2O, m.p. 175° ; $B \cdot AuCl_4$, m.p. 75° ; **B**·picronolate, m.p. 195·5° (Warren and Weiss, J. Biol. Chem. 1907, **3**, 327). For dissociation of (I) and its salts, *see* Kolthoff (Biochem. Z. 1925, **162**, 303).

***l*-Coniine**, $[\alpha]_D^{21}$ −15·3°, occurs only in small amounts; it closely resembles its *d*-isomeride. Ahrens (Ber. 1902, **35**, 1330) reports slightly different melting-points of the salts, which statement is not confirmed by Löffler and Friedrich (Ber. 1909, **42**, 107). *l*-Coniine may be obtained from conhydrine through β-coniceine (Löffler and Friedrich, *l.c.*).

N-methyl-*d*-coniine (II), $C_8H_{16}N \cdot CH_3$, $[\alpha]_D^{24 \cdot 3}$ +81·3°, b.p. 173–174°/760 mm., is a colourless oily liquid resembling coniine which may be obtained according to von Braun's method (Ber. 1905, **38**, 3108). Of the two methylconiines the *d*-form predominates. (II) is best obtained by methylation of (I) with **HCHO** and **HCOOH** (Hesse and Eichel, Ber. 1917, **50**, 1401). Methyl-*iso*-pelletierine hydrazone yields racemic methylconiine when heated to 150–170° with **Na**-ethoxide (Hess and Eichel, Ber. 1917, **50**, 1396, *cf. also* Hess, Ber. 1919, **52**, [B], 1622). $B \cdot HCl$, needles, m.p. 188°; $B_2 \cdot H_2PtCl_6$, m.p. 158°.

N-methyl-*l*-coniine, $[\alpha]_D$ −81·9°, shows a similar behaviour to (II); for further details, *see* Ahrens (*l.c.*).

Conhydrine (III), $C_8H_{17}ON$, $[\alpha]_D$ +10°, m.p. 121°, b.p. 226°/760 mm. crystallises in colourless leaflets from Et_2O. (III) is a strongly basic substance, soluble in **EtOH** and $CHCl_3$, moderately so in H_2O and sparingly in Et_2O. **N**-benzoyl-(III), m.p. 132°. Dissociation constants of (III) (*see* Kolthoff, *l.c.*).

The salts of (III) are crystalline, the aurichloride, small rhombs or prisms melts at 133°.

Pseudoconhydrine (IV), $C_8H_{17}ON$, $[\alpha]_D$ +11·0° (in **EtOH**), m.p. 105°–106° from dry ether in slender needles, or m.p. 80° from moist ether in plates, b.p. 236–236·5° (for further details and for separation from (III), *see* Löffler, Ber. 1909, **42**, 960). **N**-benzoyl-(IV), m.p. 132–133° (Späth, Kuffner and Ensfellner, *l.c.*). (IV) is a strongly alkaline base yielding crystalline salts, $B \cdot HCl$, m.p. 212–213°; $B \cdot HAuCl_4$, m.p. 133–134°; $B_2 \cdot H_2PtCl_6$ slender golden-yellow needles, m.p. 185–186°.

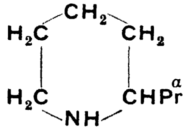
γ-Coniceine (V), $C_8H_{15}N$, optically inactive, b.p. 171–172°/746 mm., is a coniine-like oil, strongly alkaline and almost insoluble in H_2O. It is separated from (I) by von Braun's method (Ber. 1905, **38**, 3108). (V) on reduction yields rac. (I). The salts of (V) are crystalline, $B \cdot HCl$, m.p. 143°, hygroscopic; $B \cdot HBr$, m.p. 139°; $B_2 \cdot H_2PtCl_6$, m.p. 192°.

Other coniceines, α-, β- (=allylpiperidine), δ-, ε-, and ψ-coniceines are synthetic products and have been obtained in various ways from (I), bromo- or iodo-(I), conhydrine and pseudoconhydrine (for references, *see* Löffler *et al.*, Ber. 1904, **37**, 1879 ; 1905, **38**, 3326 ; 1909, **42**, 94, 107, 122, 929, 948, 3420). δ- and ε-coniceines contain a bicyclic ring-system.

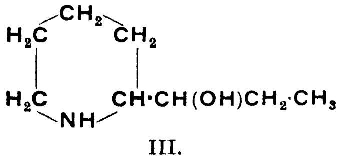
CONSTITUTION AND SYNTHESES.—(I) is 2-*n*-*propylpiperidine*, since by zinc-dust distillation of the hydrochloride, *conyrine*, *a*-*n*-propylpyridine, is obtained. (I) was first synthesised and resolved by Ladenburg (Ber. 1886, **19**. 430, 2578 ; 1889, **22**, 1403 ; 1906, **39**, 2486) and was the first synthesis of a natural alkaloid ; the method has been modified several times (Ber. 1909, **42**, 94 ; 1917, **50**, 139). More recent syntheses are recorded by Lautenschläger and Onsager (*ibid.* 1918, **51**, 602) and Koller (Monatsh. 1926, **47**, 393). For synthesis of rac. (I), *see also* Bergmann and Rosenthal (J. pr. Chem. 1932, [ii], **135**, 277), rac. (I) is also obtained by ring-opening of indolizidine with **BrCN** (Ochiai and Tsuda, Ber. 1934, **67**, 1011 ; *cf. also* Diels and Alder, Annalen, 1932, **498**, 43).

Synthesis of (II) by methylation of (I), *see above* (Passon, Ber. 1891, **24**, 1678 ; Wolffenstein, *ibid.* 1894, **27**, 2611 ; Hess and Eichel, *l.c.* 1917).

Conhydrine (III).—Willstätter (Ber. 1901, **34**, 3166) obtained *l*-piperidine-2-carboxylic acid by oxydation of (III) with CrO_3 and suggested that the hydroxyl-group in (III) must be located in the side-chain. The correct formula for (III) was first proposed by Engler and Bauer (*ibid.* 1894, **27**, 1779) and has received confirmation by the work of Hess and Eichel (*ibid.* 1917, **50**, 1386) and Späth and Adler (Monatsh. 1933, **63**, 127).



I.

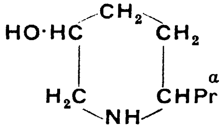


III.

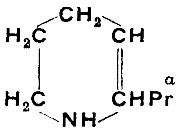
Pseudoconhydrine (IV) is a hydroxyconiine, since treatment with HI yields an iodo-(I) which on reduction forms *d*-(I). The location of the hydroxyl-group in the piperidine ring was first advocated by Löffler (*l.c.* 1909, 116); Späth, Kuffner, and Ensfellner (*l.c.* 1933) demonstrated that (IV) is 2-*n*-propyl-5-hydroxy-piperidine.

By removing the elements of H_2O from (IV) ψ-coniceine is obtained (Löffler, *l.c.* 1909, 122).

ψ-Coniceine (V).—Beside its natural occurrence (V) may be obtained by interaction of (III) and P_2O_5 or fuming HCl at 200–220°. Löffler and Tschunke (Ber. 1909, **42**, 945) suggest (V) to be Δ^a unsaturated coniine. (V) has been synthesised by Gabriel (*ibid.* 1909, **42**, 4059) by hydrolysing δ-phthalimido-butylpropylketone:



IV



V.

For colour-reactions of conium alkaloids, *see* Dilling (Pharm. J. 1909, **29**, 34, 70, 102; Biochem. J. 1909, **4**, 286). For separation of nicotine and (I), *see* Heut (Arch. Pharm. 1893, **231**, 376). For microchemical reactions of (I), *see* Cole (Philippine J. Sci. 1923, **23**, 97), Rosenthaler (Arch. Pharm. 1927, **265**, 319) and Wagenaar (B. 1929, 869). For analytical data, *see* Reichard (Pharm. Centr. **48**, 385). Krayer Arch. exp. Path. Pharm. 1931, **162**, 342) detects traces of (I) by micro-sublimation of the hydrochloride.

PHYSIOLOGICAL ACTION OF CONIUM ALKALOIDS (Henry, "Plant-Alkaloids," 2nd ed., p. 38).—All alkaloids contained in hemlock are poisonous. They produce paralysis of the motor nerve terminations and stimulation followed by depression of the central nervous system. Respiration is generally accelerated and deepened at first but eventually becomes slow and finally ceases while the heart is still strong and consciousness has just disappeared. By introduction of a double linking as in γ-coniceine the toxicity is greatly increased, whilst by the insertion of a hydroxyl-group, as in the conhydrines, it is much reduced.

Schl.

CONKURCHINE *v.* CONESSINE AND MINOR ALKALOIDS FROM HOLARRHENA SPP.

CONNELLITE. A rare mineral consisting of basic chloro-sulphate of copper with the approximate formula

$$2CuCl_2 \cdot CuSO_4 \cdot 19Cu(OH)_2 \cdot H_2O,$$

corresponding to buttgenbachite (*q.v.*) with sulphate in place of nitrate. It forms velvet-like crusts of minute hexagonal prisms with a rich blue colour. First observed in the 18th century in Cornish copper mines, it has since been found in quite small amounts at a few other localities.

L. J. S.

CONQUINAMINE *v.* CINCHONA ALKALOIDS (this vol., p. 160*c*).

CONQUININE *v.* CINCHONA ALKALOIDS (this vol., p. 169*b*).

CONSTANTAN. A nickel-copper alloy.

CONTRAMINE. Diethylammonium diethyldithiocarbamate (*British Drug Houses, London*), B.P.C.

CONVALLAMARIN and **CONVALLARIN.** Glycosides found in Convallaria, the dried inflorescence of *Convallaria majalis* L. (lily of the valley) *v.* CARDIAC GLYCOSIDES.

CONVALLATOXIGENIN *v.* CARDIAC GLYCOSIDES.

CONVALLATOXIN *v.* CARDIAC GLYCOSIDES.

CONVICINE. A glycoside found in vetch seeds, it yields on hydrolysis alloxantin, ammonia and a hexose.

CONVOLVULIN, $C_{54}H_{96}O_{27}$, m.p. 150°, is the glycosidic resin from the *Tubera Jalapæ*, known as jalap resin, and like the roots of several species of the Convolvulaceæ family, has long been used as a purgative.

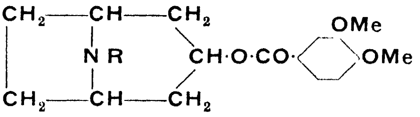
Convolvulin, on dissolving in alcohol and reprecipitating with ether (Votoček and Valentin, Coll. Trav. Chim. Tchécoslovaquie, 1929, **1**, 477) is separated into an ether soluble glycoside containing the rare sugar epirhamnose and an ether insoluble compound, rhamno-convolvulic acid, $C_{52}H_{92}O_{32},7Aq.$, which is hydrolysed to glucose (4 mol.), rhamnose (2 mol.), and convolvulinolic acid which Votoček and Prelog (Coll. Trav. Chim. Tchécoslovaquie, 1929, **1**, 55) have proved to be 2:11-dihydroxy-palmitic acid. They have suggested that in the glycoside the hydroxyl groups each carry 2 glucose molecules and 1 rhamnose molecule united to form a trisaccharide. The same hydroxy-palmitic acid is found also in *turpethin*, which contains the sugars rhodeose and glucose.

E. F. A.

CONVOLVULUS PSEUDOCANTABRICUS, ALKALOIDS OF.—*C. pseudocantabricus* Schrenk (Fam. Convolvulaceæ) is indigenous to Middle Asia; it was first investigated by Orechoff and Konowalowa (Arch. Pharm. 1933, **271**, 145), who isolated four alkaloids. Ground seeds are moistened with 25% ammonia and then percolated with benzene. The benzene is extracted with HCl, which after addition of ammonia is extracted with $CHCl_3$. On evaporation the $CHCl_3$ leaves the crude, semi-solid alkaloids (0·406%). This residue is taken up in absolute $EtOH$; by addition of alcoholic HCl a crude mixture of the hydrochlorides of convolvine (I), convolamine (II), and convolvidine (III) is obtained. The oily mother-liquor contains convolvicine (IV). (I) and (II) are separated by the different solubility of their hydrochlorides, that of (II) being easily soluble in absolute $EtOH$. By recrystallising crude (I) from light petroleum, a small insoluble fraction is obtained, from which (III) was isolated (Orechoff and Konowalowa, Ber. 1934, **67**, [B], 1153).

10 kg. of seeds yield 153·5 g. (I)·HCl, 10·7 g. (II)·HCl, 3·8 g. (III)·HCl, and a small amount of (IV) (Orechoff and Konowalowa, Ber. 1935, **68**, 814).

Convolvine (I), $C_{16}H_{21}O_4N$, m.p. 115° (from light petroleum), optically inactive, crystallises in colourless needles, easily soluble in EtOH, $CHCl_3$, and acetone, sparingly soluble in hot H_2O, Et_2O, and light petroleum. (I) is a strong base, the salts are crystalline : B·HCl, m.p. 260–261° from EtOH in which it is sparingly soluble ; B.oxalate, m.p. 265–266° from EtOH; $B\cdot HNO_3$, m.p. 212–213° from EtOH ; B-picrate, m.p. 261–263° needles from EtOH; B-chloroplatinate, m.p. 240–241° insoluble; B-chloroaurate, m.p. 217° from hot H_2O; B·methiodide, m.p. 230–231° from hot H_2O. On alkaline hydrolysis (I) yields a mixture from which Orechoff and Konowalowa (1935, *l.c.*) isolated veratric acid and nortropine, which shows that (I) is veratroyl-nortropeine and has the following structure:



(I : R=H) (II : R=Me)

By methylating (I) at the secondary *N*-atom, convolamine (II) was obtained.

Convolamine (II), $C_{17}H_{23}O_4N$, m.p. 114–115° from light petroleum, optically inactive, crystallises in stout prisms, easily soluble in EtOH, acetone, $CHCl_3$, and benzene, sparingly soluble in Et_2O and still less in light petroleum and hot H_2O. The salts are crystalline : B·HCl, m.p. 237–239° from EtOH ; B·picrate, m.p. 263–264°, decomp. plates from hot EtOH or H_2O ; B·chloroplatinate, m.p. 216–217° needles from hot dilute HCl ; B·chloroaurate, m.p. 201–202° (needles from hot dilute HCl ; B·methiodide, m.p. 257–259° colourless needles from H_2O. On hydrolysis with caustic soda (II) yields veratric acid and tropine, it has therefore the structure (II) above. The base has been synthesised by interaction of veratroyl-chloride with tropine (Orechoff and Konowalowa, 1934, *l.c.*).

Convolvidine (III), $C_{33}H_{44}O_8N_2$ (?), m.p. 192–193° (from EtOH), optically active, crystallises in small colourless needles, easily soluble in $CHCl_3$, sparingly soluble in EtOH and acetone, insoluble in H_2O, Et_2O, and light petroleum. The salts are only sparingly soluble, B·picrate, m.p. 229°–231°, easily soluble in hot acetone. On alkaline hydrolysis (III) yields veratric acid and a base not yet identified (Orechoff and Konowalowa, 1935, *l.c.*).

Convolvicine (IV), $C_{10}H_{16}N_2$, oily base, b.p. 100–125°/5 mm. or 250–260°/760 mm. Becomes yellow when exposed to the atmosphere. Easily soluble in H_2O and the usual organic solvents. B·picrate, m.p. 200–202° needles from hot H_2O. The two N-atoms apparently have a different basicity.

Orechoff points out that in the seeds 90% of the alkaloids present are (I), whereas the leaves of the plant contain (I) and (II) in about the same amount. During vegetation (II) seems to be slowly transformed into (I) (phytochemical demethylation).

Schl.

COOK'S ALLOY. An alloy containing 43% zinc and 57% antimony.

COOPERITE. Platinum sulphide, PtS, as tetragonal crystals, with the unit-cell dimensions *a* 4·91, *c* 6·10Å. As minute grains it appears to be the main platinum-bearing component of the concentrates from the Bushveld *norite*, Transvaal. When first described by R. A. Cooper (J. Chem. Met. Soc. S. Africa, 1928, **28**, 283 ; 1929, **4**, 268, 275) it was thought to be PtS_2 and isomorphous with *sperrylite* [$PtAs_2$] ; later H. Schneiderhöhn (1929) described it as orthorhombic and isomorphous with *marcasite* [FeS_2] ; while one crystal described by H. R. Adam (1931) as cooperite has since been proved to be *laurite* [RuS_2]. This is a case where chemical analyses have been made on mixtures, and crystallographic determinations have been made on single grains picked out from the mixture. By examining each grain separately by X-ray methods it has been possible to select sufficient homogeneous material for chemical analysis (F. A. Bannister, Min. Mag. 1932, **23**, 189). The name cooperite was first used in 1869 for a variety of serpentine ; it is also a trade-name for an alloy, Ni-Zr-W, etc., used for cutting tools.

L. J. S.

CO-ORDINATION COMPOUNDS.—When used in a chemical sense the term co-ordination is applied to a mode of atomic linking first recognised in 1893 by Alfred Werner, who subsequently devoted the remaining years of his life to a systematic study of co-ordination compounds. The hypotheses proposed by him in explanation of the results of his researches are embodied in the co-ordination theory, which affords a simple and comprehensive explanation of the chemical constitutions of the most diverse types of complex metallic salts, including aquo- and ammino- derivatives, mordant dyes, and many representative minerals. Even before Werner's time numerous chemical compounds were known, the formation of which could not be explained on the older theories of valency. Such substances, often termed "molecular compounds," were generally formed from simpler compounds in which the combining elements had exercised their valencies in accordance with their position in the periodic classification. For instance, hydrogen chloride, a combination of univalent hydrogen and chlorine in atomic proportions, combines with ammonia, a compound of tervalent nitrogen with three univalent hydrogen atoms to form the molecular compound ammonium chloride. This secondary combination of hydrogen chloride and ammonia was formerly regarded as being due to the possession by these substances of a "residual affinity," a force which was then considered to differ from that of valency.

Werner examined a large number of metallic ammines, compounds of similar type to ammonium chloride, although generally more complex in molecular structure, and showed that they could all be formulated on a new principle. The underlying idea of Werner's theory was that the combining powers of an atom depended not only on the nature but also on the number of atoms or groups with which it could become associated. It is this number, which Werner called the "co-ordination number," rather than the valency in terms of hydrogen equivalents, which gives a measure of the total combining power of the element. A general survey of complex metallic salts shows that the co-ordination number is most frequently 6, sometimes 4, and less often 8 or other values.

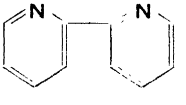
In writing graphic formulæ in accordance with the co-ordination principle the convention is usually adopted of enclosing the central nuclear element and its associating units within a square bracket, which thus contains all the elements implicated in the co-ordination complex or inner sphere. It should, however, be explained that this co-ordination principle supplements but does not supersede the older conceptions of valency. Any accurately written co-ordination formula can be dissected into constituent parts which are expressible in terms of integral valencies. The verification is readily seen in the case of ammonium chloride and is equally applicable in the following instances: $[Cr6NH_3]Cl_3$ and $K_4[Fe(CN)_6]$, where the generators of the complex ammine are $CrCl_3$ and NH_3, and those of the complex cyanide are KCN and $Fe(CN)_2$. These two compounds furnish examples of the 3 types of atomic linkings recognised by chemists: (i) a non-polar, non-ionised link as exemplified in the combination of nitrogen and hydrogen in ammonia or in the attachment of carbon to nitrogen in the cyanide radical; (ii) a polar or ionised link between the oppositely charged ions of a salt as in dissolved $CrCl_3$ or KCN, and also between the complex cation $[Cr6NH_3]$ and the 3 chlorine ions or between the complex anion $[Fe(CN)_6]$ and the 4 potassium ions; (iii) the co-ordination link postulated by Werner as existing between chromium and 6 ammonia or between iron and 4 cyanogen groups.

In 1857 a remarkable foreshadowing of Werner's views was published by Gibbs and Genth in a research on ammonio-cobalt bases wherein they referred to the cobalt atom as "hexatomic," although they also recognised that the combining capacity (principal valency) of this atom was 3. They referred to the inner co-ordination sphere of cobalt with 6 associating units as the "conjunct" ("Smithsonian Contribution to Knowledge," Washington, 1857, IX).

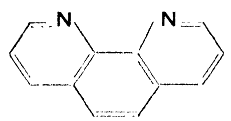
MANIFOLD ASSOCIATING GROUPS.—In the foregoing examples, $[Cr6NH_3]Cl_3$ and $K_4[Fe(CN)_6]$, the ammonia and cyanogen groups occupy only one position within the co-ordination sphere, and a similar degree of association is manifested by the halogens, water, hydroxyl groups, oxygen, pyridine, methylamine, dialkyl- or diaryl-sulphides, phosphines, arsines, and many other molecular species. But co-ordination is by no means confined to such single associating units. There are a great many examples of compounds which contribute 2, 3, or 4 units to the co-ordination complex.

Chelate Groups.—Compounds such as ethylenediamine and radicals such as the oxalate group C_2O_4, which each function in the co-ordination sphere as two associating units or doubly bound groups, often to form exceedingly stable co-ordination complexes, have been grouped by Morgan (J.C.S. 1920, **117**, 1457) under the convenient general term of chelate groups [from χηλή (Greek), chela (Latin), chely, (English)] the crab's pincer claw. Certain of these chelate groups have played an important part in the demonstration of stereochemical structure of co-ordination compounds.

2:2′-Dipyridyl (I) and *o*-phenanthroline (II) furnish examples of such chelate groups, both of which were employed by Werner in the demonstration of octahedral structure.



"Dipy."
I.



"Phenan."
II.

Blau had previously prepared the dark red tris-2:2′-dipyridyl ferrous bromide

$$[Fe3dipy]Br_2,6H_2O$$

(Monatsh. 1898, **19**, 647), and Werner (Ber. 1912, **45**, 433) showed that this salt could be resolved into optically active forms. Morgan and Burstall have since resolved the analogous pale red nickel salts, $[Ni3dipy]Cl_2,6H_2O$, into dextro- and lævo-components (J.C.S. 1931, 2214). The corresponding orange red bivalent ruthenium salt $[Ru3dipy]Cl_26H_2O$ has also proved sufficiently stable for resolution into optically active forms (Burstall, J.C.S. 1936, 173).

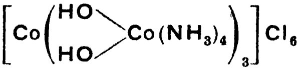
These 2 chelate bases have also proved useful in demonstrating the bivalency of silver. Hieber and Mühlbauer (Ber. 1928, **61**, [B], 2149) have obtained bivalent silver salts such as

$$[Ag2phenan]S_2O_8 \text{ or } X_2,$$

where $X = HSO_4$, NO_3, ClO_3, or ClO_4, and Morgan and Burstall (J.C.S. 1930, 2594) have prepared the salts $[Ag2dipy]S_2O_8$ or $(HSO_4)_2$, while Barbieri (Atti R. Accad. Lincei, 1932, **16**, 44) has obtained the derivatives

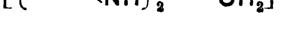
$$[Ag2dipy](NO_3)_2 \text{ or } (ClO_4)_2.$$

Chelate groups need not be organic, for Werner was able to show that the basic cobaltic salt, dodecamminohexoltetracobaltic chloride containing 3 chelate groups $\{(HO)_2Co4NH_3\}$ is resolvable into optically active forms (Ber. 1907, **40**, 2113; 1914, **47**, 3087).



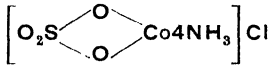
$$\left[Co\left(\begin{matrix}HO\\HO\end{matrix}>Co(NH_3)_4\right)_3\right]Cl_6$$

In more recent times, Mann (J.C.S. 1933, 412) has isolated optically active components of a complex rhodium salt containing sulphamide.

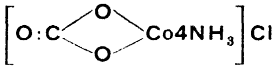


$$\left[\left\{SO_2<\begin{matrix}NH\\NH\end{matrix}\right\}_2 Rh\begin{matrix}\swarrow OH_2\\ \nwarrow OH_2\end{matrix}\right]Na$$

Whereas many chelate groups are attached to a metal with formation of a stable five-membered ring system, the foregoing sulphamide derivative contains a four-membered ring. Other examples of this type of chelation are present in complex sulphates and carbonates such as



and



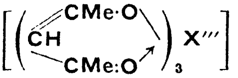
and also among many polynuclear compounds (*v. infra*).

Six-membered chelate rings are very plentiful among co-ordination compounds and include derivatives of 1:3-diaminopropane,

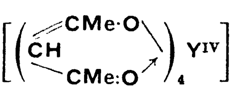
$$H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

of malonic acid, $HOOC{\cdot}CH_2{\cdot}COOH$, and the characteristic and notable metallic complexes of acetylacetone.

Metallic Acetylacetones.—The univalent radical $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3){\cdot}O$— derived from acetylacetone furnishes an important chelate group, and similar groups are derived from the homologous β-diketones and analogous β-keto esters. This acetylacetone radical enters into combination with many of the metals as a doubly bound group and gives rise to cyclic co-ordination compounds of remarkable stability, often having other exceptional properties such as unusual colour, solubility in organic media, and volatility without decomposition. In the last respect this chelate group may be said to give wings to metals. Aluminium and scandium acetylacetones represented by the general formula (I) (where $X''' = Al$ or Sc) are volatile without decomposition.



I.

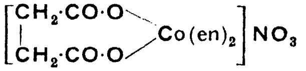


II.

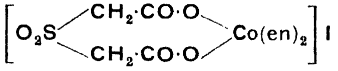
Thorium acetylacetone containing four of these chelate groups has also been distilled. Compounds of similar type have been obtained from zirconium, hafnium, and from quadrivalent cerium (II, where $Y^{IV} = Th, Zr, Hf$, or Ce^{IV}). The acetylacetone radical " Ac " and its homologues co-ordinate with the elements boron, silicon, germanium, titanium, tin and zirconium conferring ionic properties on the complex so that polar compounds arise. The boronium and siliconium compounds studied by Dilthey (Annalen, 1905, **344**, 300 ; Ber. 1903, **36**, 923, 1395, 3207), and Rosenheim, Löwenstamm and Singer (*ibid.* 1833) are of the types [B“Ac”$_2$]FeCl$_4$ or AuCl$_4$; [B“Ac”$_2$]$_2$PtCl$_6$; [Si“Ac”$_3$]FeCl$_4$ or AuCl$_4$; [Si“Ac”$_3$]$_2$PtCl$_6$. Following on silicon the various modes of interaction with acetylacetone exhibited by other elements of the fourth periodic series are shown in the following series :

[Ti“Ac”$_3$]FeCl$_4$; [Ge“Ac”$_3$]CuX$_2$; [Ge“Ac”$_2$X$_2$]; [Sn“Ac”$_2$X$_2$] ; [Zr“Ac”$_3$]Cl ; [Zr“Ac”$_4$] ; [Hf“Ac”$_4$] ; [Ce“Ac”$_3$] ; [Ce“Ac”$_4$] ; [Pb“Ac”$_2$] ; [Th“Ac”$_4$].

Although the vast majority of chelate rings are those of five and six members, there are a few examples of seven- and even eight-membered rings. The former including carboxylic acids such as succinic, maleic, and itaconic acids, are exemplified by the cobaltammine (I) :



I.



II.

("en" – ethylenediamine.)

(Duff, J.C.S. 1921, **119**, 385) whereas the eight-membered ring is present in the complex salt of sulphonyldiacetic acid (II) (Price and Brazier, J.C.S. 1915, **107**, 1367).

Tridentate Groups.—Threefold associating groups have been recognised such as $\alpha\beta\gamma$-triaminopropane = "tpn," which co-ordinates with cobalt and rhodium as a tridentate radical to furnish the complex salts [Co2tpn]Cl$_3$ and [Rh2tpn]I$_3$ (Mann and Pope, Proc. Roy. Soc. 1925, (A), **107**, 80), and 2:2′:2″- tripyridyl or di-2-pyridyl-2:6-pyridine ("tripy") which forms two series of salts containing respectively 2 and 1 molecules of the triamine. The former series is exemplified by the purple ferrous salt [Fe2tripy]Br$_2$I and 4H$_2$O and the latter by the stable red platinous compound

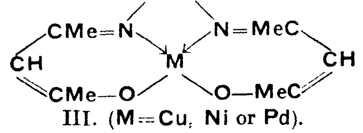
[PtCltripy]Cl$_2$, 2 and 3H$_2$O

(Morgan and Burstall, J.C.S. 1932, 22; 1934, 1498).

Quadridentate Groups.—A fourfold associating unit is furnished by the bivalent radical of ethylenediaminebisacetylacetone,

$$\{CH_2{\cdot}N{:}C(CH_3){\cdot}CH{:}C(OH){\cdot}CH_3\}_2 = ec,$$

which forms remarkably stable complexes $R^{II}ec$ with copper, nickel, and palladium (III).



III. (M = Cu, Ni or Pd).

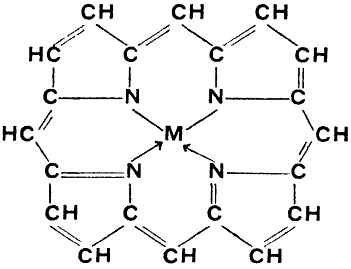
In the absence of air the two former compounds may be boiled without decomposition. The cobaltic complex salts [Coec2NH$_3$]Br exist in stereoisomeric forms (Morgan and Main Smith, J.C.S. 1925, **127**, 2030; 1926, 912). Tri-β-aminoethylamine $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$ = "tren" also behaves as a fourfold associating compound and gives rise to the platinum salts [Pttren]I$_2$ and [PtCl$_2$tren]Cl$_2$ (Mann and

Pope, Proc. Roy. Soc. 1925, **109**, A, 455), and to the cobaltic derivative

$$[(SCN)_2Cotren]SCN,H_2O$$

(Mann, J.C.S. 1929, 409).

Fourfold co-ordinating units of a different type are represented in the naturally occurring pigments chlorophyll and hæmin (*v. infra*), which possess a constitution based on that of porphin, the parent of the series, which yields metallic derivatives of the type IV (Fischer and Gleim, Annalen, 1935, **521**, 157; Rothemund, J. Amer. Chem. Soc. 1936, **58**, 625).

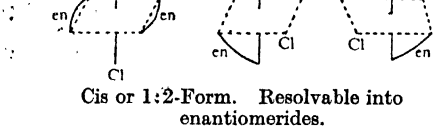


IV. ($M = Mg$, Cu, or FeCl)

Stereochemical Demonstration of Co-ordination.—The prevalence of co-ordination numbers 4 and 6 suggested that co-ordination compounds had a spatial arrangement of their associating units corresponding respectively with the tetrahedron and octahedron. Moreover, many compounds with a co-ordination number of 4 possess a planar distribution of addenda with the metallic atom at the centre of a flat four-point figure.

Octahedral Structure.—Werner predicted that cobaltammines containing co-ordination complexes of the type $[CoA_2B_4]$ would exist in two stereo-isomeric forms, and that if the $4NH_3$ groups of example $[CoBr_24NH_3]Br$ were replaced by 2 mols. of ethylenediamine, "en" $= NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, then one of the two isomeric salts $[CoBr_22en]Br$ would be resolvable into optically active forms (enantiomers). His verification of the latter prediction in 1911 gained world-wide acceptance of the co-ordination hypothesis and raised it to the level of a general theory of chemical combination and molecular structure.

This demonstration was first accomplished with chloroamminodiethylenediaminocobaltic chloride $[NH_3CoCl2en]Cl_2$, which exists in 2 isomeric modifications depending on the spatial arrangements of associating units in the co-ordination sphere as illustrated by the following figure :



Cis or 1:2-Form. Resolvable into enantiomerides.

The racemoid cis-chloride was converted into *d*-bromocamphorsulphonate when the *dd*-salt was found to be more sparingly soluble than the *ld*-salts. The two *d*-bromocamphorsulphonates were then separately converted into bromides which in 1% aqueous solution gave $[\alpha]_C \pm 43°$, corresponding with molecular rotation

$$[M]_C = \pm 168 \cdot 7°$$

(C line $656 \cdot 3 m\mu$). These two optically active salts were very stable, showing no tendency to racemise (Werner, Ber. 1911, **44**, 1887).

Other interesting complex salts, which exhibit optical activity, possess the structures

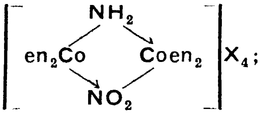
$$[M3dipy]Cl_2,6H_2O$$

(where M = Fe, Ru, Os, Ni, and dipy = 2:2′-dipyridyl), $[M3en]Cl_3$ (where M = Co, Cr, Rh, and en = ethylenediamine) and

$$[M(C_2O_4)_3]K_3$$

(where M = Al, Cr, Fe^{III}, Co^{III}, Ir, and Rh). In these salts the chelate groups 2:2′-dipyridyl, ethylenediamine or oxalate radical span the six points of an octahedron with the metal at the centre.

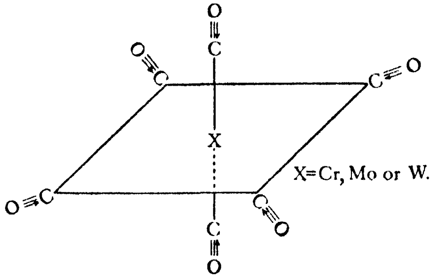
Representative co-ordination compounds employed in subsequent demonstrations were the following : $[Co2NH_32en]Br_3$; $[Co3en]Cl_3$;



$$\left[en_2Co \overset{NH_2}{\underset{NO_2}{\rightleftarrows}} Coen_2 \right] X_4 ;$$

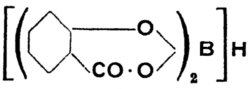
obtained in meso and racemoid forms, $[CrCl_32en]X$; $[Cr3en]X_3$; $[Cr(C_2O_4)_3]K_3$; $[Rh3en]Cl_3$. Optically active forms of compounds having octahedral symmetry have been isolated in the case of the following elements as the central atom : aluminium, arsenic, chromium, cobalt, iron, nickel, iridium, platinum, rhodium, ruthenium and osmium.

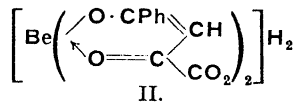
In recent years, X-ray analysis has been increasingly used in the determination of structure among co-ordination compounds and a considerable number have been shown to possess an octahedral distribution of valencies by this means. The compounds $K_4[Fe(CN)_6]$, $K_2[PtCl_6]$, $[Co6NH_3]Cl_3$, $K_2[OsCl_5NH_3]$, $[RhCl5NH_3]Cl_2$ represent octahedral structures determined by X-rays. As final examples of octahedral co-ordination compounds the carbonyls of chromium, molybdenum and tungsten $M(CO)_6$ (M = Cr, Mo, or W) may be cited since these compounds owe their existence entirely to co-ordinate links between carbon monoxide and the metal atom. The arrangement of addenda is indicated in the folowing figure (*cf.* Hieber, Romberg and Mühlbauer, Z. anorg. Chem. 1935, **221**, 321–349).



Tetrahedral Structure.—Even before the recognition by Werner of the co-ordination link a demonstration of tetrahedral structure had been made in the case of elements other than carbon. In 1899 Pope and Peachey showed that quaternary ammonium salts of the type $[\mathrm{Nabcd}]^+\mathrm{X}^-$ could be resolved into optical antipodes. Amine oxides [NabcO] were obtained in optically active forms by Meisenheimer in 1908, and in 1911 this observer and Lichtenstadt prepared optically active phosphine oxides PabcO.

Since the enunciation of the co-ordination theory, tetrahedral symmetry has been demonstrated in the case of several other elements. Borosalicylic acid (I) has yielded a strychnine salt with an optical activity due to the boron complex (Böeseken and Meulenhoff, Proc. K. Akad. Wetensch. Amsterdam, 1924, **27**, 174); and Mills and Gotts resolved the beryllium derivative of benzoylpyruvic acid (II) and employed similar means in demonstrating tetrahedral symmetry in zinc compounds (J.C.S. 1926, 3121).

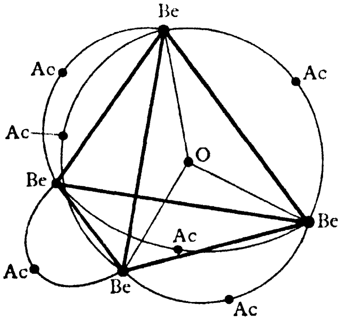

I.


II.

The tetrahedral distribution of associating units round oxygen is indicated by the work of Bragg and Morgan (Proc. Roy. Soc. 1923, **104**, A, 437) on basic beryllium acetate,

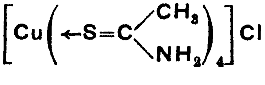
$$\mathrm{Be_4O(CH_3{\cdot}CO_2)_6}\ \text{(III)}$$

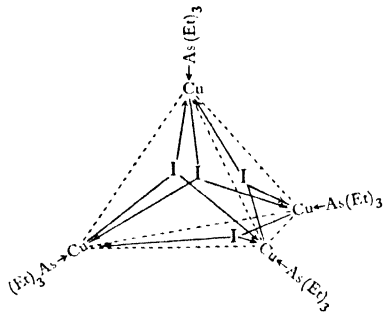
and its homologues (Morgan and Astbury, *ibid.* 1926, **112**, 441).



III.

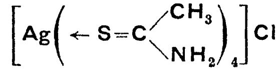
Significant results have been obtained from determinations of structure by means of X-ray analysis. A tetrahedral arrangement of molecules in cuprous compounds with a co-ordination number of 4 has been demonstrated for the well-known cyanide $\mathrm{K_3[Cu(CN)_4]}$ and the thio-acetamide salt by Cox, Wardlaw and Webster (J.C.S. 1936 775) whereas 4-covalent cupric derivatives (*v. infra*) are planar. A structure of novel type has been found by Mann, Purdie and Wells (J.C.S. 1936, 1503) for the compound of cuprous iodide with triethylarsine, $[(\mathrm{Et})_3\mathrm{As}\rightarrow\mathrm{CuI}]_4$. The arrangement is tetrahedral with copper atoms at the four vertices of the figure whereas the iodine atoms are centred but situated rather above the four faces of the tetrahedron (IV).


$$\left[\mathrm{Cu}\left(\leftarrow\mathrm{S}=\mathrm{C}\begin{matrix}\mathrm{CH_3}\\ \mathrm{NH_2}\end{matrix}\right)_4\right]\mathrm{Cl}$$

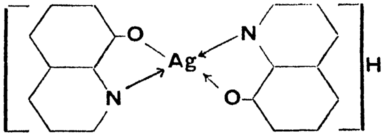


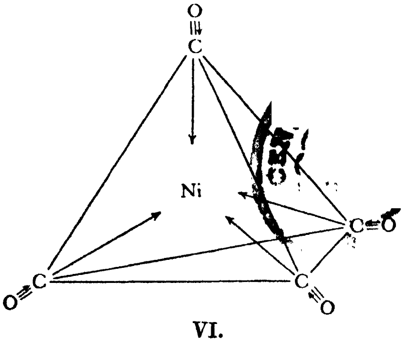
IV.

Univalent silver derivatives with a co-ordination number of 4 are also tetrahedral as exemplified by


$$\left[\mathrm{Ag}\left(\leftarrow\mathrm{S}=\mathrm{C}\begin{matrix}\mathrm{CH_3}\\ \mathrm{NH_2}\end{matrix}\right)_4\right]\mathrm{Cl}$$

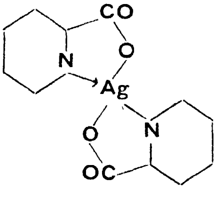
Whilst Hein and Regler (Ber. 1936, **69**, [B], 1692) obtained indications of optical resolution with the silver derivative (V) of 8-hydroxyquinoline, which must, therefore, be tetrahedral. Other 4-covalent compounds of tetrahedral structure are the cyanides $\mathrm{K_2[M(CN)_4]}$ (M = Zn, Cd or Hg) and the well-known and technically important nickel carbonyl $\mathrm{Ni(CO)_4}$ (VI) (Sutton, New and Bentley, J.C.S. 1933, 652 ; Brockway and Cross, J. Chem. Phys. 1935, **3**, 828).


V.



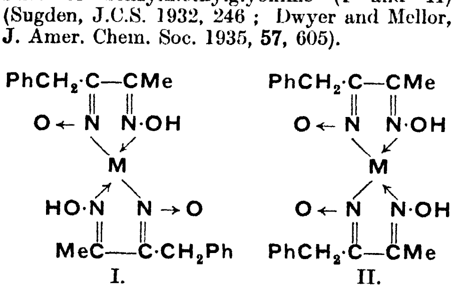
VI.

Planar Structures.—In the foregoing survey of molecular structure among co-ordination compounds it was noted that when manifesting their fundamental univalency, copper and silver exhibited a tetrahedral arrangement of addenda in their fourfold co-ordinated compounds. It has now been found that in their higher valent states, copper, silver, and gold exhibit a planar configuration when the co-ordination number is 4. By X-ray analysis cupric acetylacetone, $Cu(C_5H_7O_2)_2$ has been shown to be planar (Cox and Webster, J.C.S. 1935, 731) and the compounds $[CuCl_2,2H_2O]$ and $[CuCl_22py]$ have also been shown to be similarly constituted (Cox, Sharratt, Wardlaw and Webster, J.C.S. 1936, 129 ; Harker, Z. Krist. 1936, **93**, 136). The planar arrangement among bivalent silver derivatives has been demonstrated by X-ray study of the argentic derivative of picolinic acid (Cox, Wardlaw and Webster, J.C.S. 1936, 775)



and tervalent gold in potassium auribromide $K[AuBr_4]2H_2O$ has a planar distribution of 4 bromine atoms round it (Cox and Webster, J.C.S. 1936, 1635).

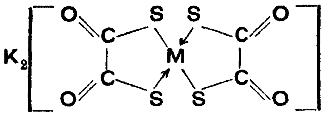
Among tin and lead compounds, it is the lower valent compounds such as $K_2[SnCl_4]2H_2O$ and $[PbCl_32SC(NH_2)_2]$ which have a planar structure in contrast to the tetrahedral arrangements of stannic derivatives represented by SnI_4 and $Pb(C_6H_5)_4$ in which a fundamental quadrivalency is manifested (Cox, Shorter and Wardlaw, Nature, 1937, **139**, 72). A considerable amount of work has also been carried out on planar compounds containing elements of group VIII in the Periodic Classification. Chemical evidence in support of planar configurations has been obtained by the isolation of *cis-* and *trans-* forms of the nickel and palladium salts of benzylmethylglyoxime (I and II) (Sugden, J.C.S. 1932, 246 ; Dwyer and Mellor, J. Amer. Chem. Soc. 1935, **57**, 605).



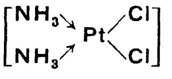
I. II.

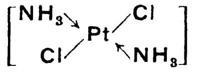
trans (M = Ni or Pd.) *cis*

The complex dithio-oxalates of nickel, palladium and platinum (III) have been shown to be planar by X-ray analysis (Cox, Wardlaw and Webster, J.C.S. 1935, 1475). Co-ordinated bivalent platinum derivatives have, in some cases, been regarded as planar since the inception of the Co-ordination Theory by Alfred Werner who concluded that the two platosammines $(PtCl_22NH_3)$ were *cis-* and *trans-* isomerides.

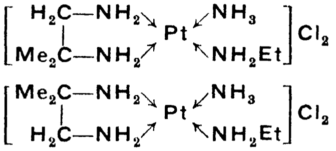


III. (M = Ni, Pd or Pt.)





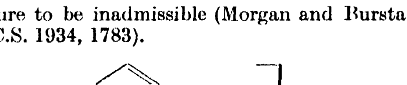
Recent X-ray analyses support this conclusion and extend planar configurations to $K_2[PtCl_4]$, $[Pt4NH_3]Cl_2,H_2O$, $[PtCl_2,2SMe_2]$, and many other compounds including the corresponding palladium derivatives. Chelated platinammines also conform to a planar distribution of valencies, since Drew and Head (J.C.S. 1934, 221) have obtained the two isomeric dichlorides :



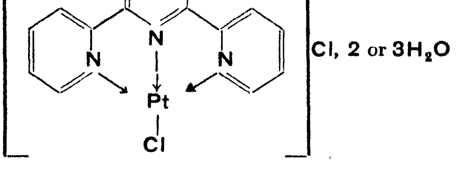
A similar pair have also been prepared containing 2 mols. of *iso*butylenediamine

$$[Pt(NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2)_2]Cl_2, 1 \text{ or } 2H_2O.$$

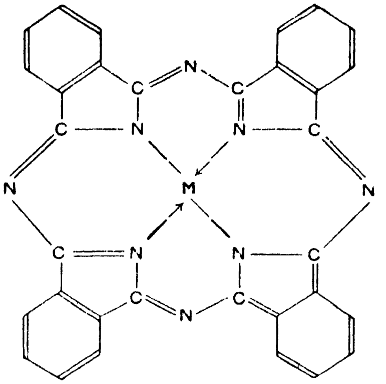
Another elegant proof of the planar arrangement of addenda among platinammines has been furnished by Mills and Quibell (J.C.S. 1935, 839), who prepared a salt with the following cation :



and have resolved it into optically active forms which could not exist if the ion were tetrahedral. A final example of planar platinous salts is a derivative containing 2:6-di-2′-pyridyl-pyridine, in which a tetrahedral arrangement of the tridentate addendum is seen from the following figure to be inadmissible (Morgan and Burstall, J.C.S. 1934, 1783).



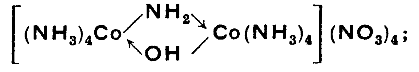
A noteworthy contribution to the stereochemistry of co-ordination compounds was made by the discovery of the phthalocyanines, a series of metallic complexes of unusual structure and great stability, conveniently produced by heating the metal or its chloride with phthalonitrile (1:2-dicyanobenzene), they sublime, in many cases, without decomposition at high temperatures. The planar configuraton of the phthalocyanines is confirmed by X-ray examination. The foregoing formula suggests that the organic molecule functions as a fourfold associating unit (quadridentate group). The copper derivative is an important pigment now known commercially as Monastral Fast Blue B.S. (Linstead and co-workers, J.C.S. 1934, 1016–1033; 1936, 1719–1738). The corresponding naphthalocyanines have also been prepared from 1:2-dicyanonaphthalene (*idem* J.C.S. 1936, 1744).



M = Cu, Be, Mg, Ca, Zn, Cd, Ba, Sn^{II}, Pb, Fe, Mn, Co, Ni, Pt, AlCl, Vo, $Sn^{IV}Cl_2$.

Polynuclear Compounds. — Co-ordination compounds may contain 2 or more nuclear atoms in the complexes. Among non-polar substances are basic beryllium acetate Be_4OAc_6 and its homologues. From a very large group of complex polynuclear salts the following comparatively simple examples are selected :

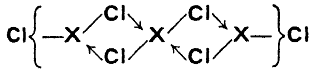
$[en_2Cr(OH)_2Cr\ en_2]Br_4$;



$$\left[(\mathrm{NH_3})_4\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co}(\mathrm{NH_3})_4\right](\mathrm{NO_3})_4;$$

$[Cu_25tu](NO_3)_22Aq.$; $[Cu_37tu](NO_3)_3$;
$[Cu_25etuH_2O](NO_3)_2,3Aq.$; and
$[Ag_23etu](NO_3)_2$;

where " tu "=thiourea and " etu "=ethylene thiourea. A series of remarkable chloroacids has the general formula $[H_2O{\cdot}X_3Cl_7]H,3Aq.$ where X=Mo, Ta, or W (and probably Nb). These complex acids are derived from the chlorides $(XCl_2)_3$ or X_3Cl_6, which contain a stable inner core X_3Cl_4. Accordingly the structure



$$\mathrm{Cl}\left\{-\mathrm{X}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\mathrm{X}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\mathrm{X}-\right\}\mathrm{Cl}$$

has been proposed for the parent chlorides. The complex phospho-molybdic and tungstic acids are limiting examples of a numerous and diversified class of hetero-polynuclear acids (" hetero-polybasic acids ") ; their salts may be written as $[PO_412XO_3]R_3$, nAq., where X=Mo or W and R=Na, K or NH_4. Moreover, phosphorus may be replaced by arsenic. These derivatives contain a basic tetrahedron with phosphorus at the centre and 4 oxygen atoms at the points of the solid figure. On this simple structure is built up a symmetrical arrangement of 12 interlocking WO_6 units which are divided up into 4 groups of 3 octahedra. In each WO_6 group, 1 oxygen atom is held in common with the phosphorus atom (and is also shared with 2 other WO_6 groups), 2 are shared with tungsten atoms of its own group of 3 octahedra, 2 with metallic atoms of other groups of octahedra, and 1 is unshared by other atoms. A similar arrangement is exhibited by the acids $H_4[MX_{12}O_{40}]$, $H_5[BW_{12}O_{40}]$ and $H_6[H_2W_{12}O_{40}]$, where M=Si, Ge, and X=Mo and W (Keggin, Proc. Roy. Soc. 1934, **144**, 75 ; Illingworth and Keggin, J.C.S. 1935, 575).

Other Co-ordination Numbers.—In addition to co-ordination numbers 4 and 6, which suggest respectively tetrahedral and octahedral arrangements, there are metallic complexes and complex salts containing 8 associating units such as the acetylacetones of cerium, zirconium and thorium already mentioned, and salts with eightfold complex cations as

$[Cu8NH_3][Pt(CNS)_4]$,
$[Mg8H_2O][Th(NO_3)_6]$

or with an eightfold anion as in $K_4[Mo(CN)_8]$, which gives rise to the free acid

$H_4[Mo(CN)_8],6H_2O$

There is, however, no evidence as to the spatial arrangement of associating units in these compounds. In a study of the alums which were formerly supposed to indicate a co-ordination number of 12, the tervalent metal is surrounded by 6 mols. of water, $[M^{III}6H_2O]M^{I}(SO_4)_26H_2O$. The arrangement of the remaining water molecules differs slightly according to the size of the univalent metallic ion (Lipson, Proc. Roy. Soc. 1935, **151**, 347).

Reference should be made to compounds exhibiting odd co-ordination numbers (C.N.) :

C.N. Three.—This number is displayed in a series of oxy- and thio-acids in which the principal valency of the central element may vary from three to five : borates $[BO_3]$, carbonates $[CO_3]$, thiocarbonates $[CS_3]$, nitrates $[NO_3]$, and sulphites $[SO_3]$, meta acids of phosphorus, antimony, vanadium, columbium and tantalum $[XO_3]$, chlorates $[ClO_3]$, bromates $[BrO_3]$ and iodates $[IO_3]$.

C.N. Five.—Cupric halides co-ordinated with 5 mols. of ammonia, pyridine, etc., *e.g.*

$[Cu5base]X_2$.

C.N. seven, of which series the analytically important K_2TaF_7 is the most outstanding example. It is noteworthy that tantalum also gives a more regular type K_3TaF_8.

Electronic Interpretation of Co-ordination.—The electronic conception of matter gives precision to the co-ordination theory since it offers a simple explanation of the three manifestations of valency now recognised by chemists : (1) Electrovalency with polar or ionisable links as in the oppositely charged ions of sodium chloride, $\overset{+}{\mathrm{Na}}\mathrm{Cl}^-$, ammonium chloride $\mathrm{NH_4}^+\mathrm{Cl}^-$ or hexamminocobaltic chloride

$$[\mathrm{Co6NH_3}]^{+++}\mathrm{Cl_3}^{---}$$

(2) Covalency with non-polar non-ionisable links such as those which unite carbon to hydrogen in methane, nitrogen to hydrogen in ammonia, or carbon to nitrogen in cyanogen. (3) The co-ordinate link of Werner such as combines cobalt with ammonia in the foregoing cobaltammine.

The driving force discernible in these three types of linking is a tendency on the part of each of the combining atoms to assume the electronic configuration of the nearest inert gas. Of these gases helium has 2 electrons, but each of the others has outer groups of 8 electrons—the octet.

(1) *Electrovalency* (*the Polar Link*).—In forming sodium chloride, sodium gives its single outer electron to chlorine, and by this exchange the sodium ion acquires the electronic configuration of neon while the chlorine ion completes its octet, thus resembling argon.

(2) *Covalency* (*the Non-polar Link*).—The two combining atoms share electrons as in methane, which contains 4 covalent links. Each of these 4 links includes 2 electrons, 1 contributed by carbon and 1 by hydrogen, so that in methane carbon has assumed the electronic structure of neon and each hydrogen has acquired the 2 electrons characteristic of helium. This type of non-polar link to which each of two combining elements contributes 1 electron is typical of the non-polar compounds of organic chemistry.

(3) *Co-ordination Covalency* (*the Co-ordinate Link*).—This mode of attachment differs from the foregoing type of co-valency or non-polar link in that both electrons are furnished by one of the combining elements (Sigdwick, J.C.S. 1923, **123**, 725). This type of combination is exemplified in the luteocobaltammine

$$[\mathrm{Co6NH_3}]\mathrm{Cl_3},$$

wherein the tervalent cobalt ion which differs electronically from krypton by 12 electrons completes its quota of electrons by co-ordinating with 6 mols. of ammonia. In this combination each nitrogen atom contributes 2 shared electrons, so that within the co-ordination sphere the cobalt has acquired the electronic configuration of krypton, whereas each nitrogen retains the octet of neon.

By a similar process of reasoning it may be shown that this electronic equality holds in the case of purpurocobaltammine $[\mathrm{CoCl5NH_3}]\mathrm{Cl_2}$, and also generally among co-ordination compounds of tervalent cobalt. The fact that the acquirement of a complete octet by cobalt coincides with the symmetrical octahedral grouping of 6 associating units affords an explanation of the existence of so many well-defined members of this cobaltammine series and accounts for the stability of complex cobaltic salts such as $\mathrm{K_3[Co(NO_2)_6]}$ and $\mathrm{Na_3[Co(CN)_6]}$.

This coincidence is also apparent in the case of the platinammine compounds of tetradic platinum of the following series : $[\mathrm{Pt6NH_3}]\mathrm{Cl_4}$; $[\mathrm{PtCl5NH_3}]\mathrm{Cl_3}$; and intermediate types to $[\mathrm{PtCl_42NH_3}]$; $[\mathrm{PtCl_5NH_3}]\mathrm{K}$; and $[\mathrm{PtCl_6}]\mathrm{K_2}$.

As regards co-ordination compounds, chromium resembles cobalt, giving rise to numerous ammines and complex salts, but in this instance the development of octahedral symmetry does not coincide exactly with the acquirement by the central metallic atom of an electronic structure characteristic of krypton. Throughout the series there is a deficiency of 3 electrons, but, nevertheless, many individuals of this numerous group of co-ordinated chromic derivatives show remarkable stability with similar phenomena of stereoisomerism and optically active enantiomerides.

Certain of the co-ordination compounds of nickel and copper show the opposite tendency in the combination of these bivalent metals with 6 associating units. For if each unit should contribute 2 electrons, then there would be an excess of electrons over the number required to endow the metallic radical with the electronic structure of krypton. Nevertheless, such a complex salt as $[\mathrm{Ni3dipy}]\mathrm{Cl_2}$ is sufficiently stable to be resolvable into optically active enantiomerides.

This interpretation of co-ordination as taking place with 2 electrons does not, however, exclude a 1-electron covalent link. In the copper derivative (*v. supra*) of ethylenediaminobisacetylacetone (Cuec) the cupric ion is still 1 electron short of the krypton structure which, however, is acquired when this compound co-ordinates further with water or ethylenediamine hydrate to form respectively $[\mathrm{H_2OCuec}]$ and $[\mathrm{ecCuNH_2{\cdot}C_2H_4{\cdot}NH_3}]\mathrm{OH}$, the latter dehydrating to

$$[\mathrm{ecCuNH_2{\cdot}C_2H_4{\cdot}NH_2Cuec}]$$

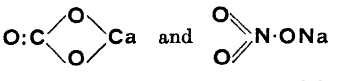
These addenda are more loosely held than the original "ec," a circumstance which suggests the single link. In the nickel complex [Niec] the metal is still 2 electrons short of the krypton structure, and this unsaturation is revealed by the formation of ammino- and ethylenediamino-compounds $[\mathrm{2NH_3Niec}]$ and

$$[\mathrm{C_2H_4(NH_2)_2Niec}]$$

(Morgan and Main Smith, J.C.S. 1925, **127**, 2030 ; 1926, 912).

NOTEWORTHY EXAMPLES OF CO-ORDINATION PHENOMENA.

A Wider Basis for the Principle of Isomorphism.—The older principle of integral valency led to structural formulæ which afforded no explanation of the isomorphism of calcite and sodium nitrate which were formerly formulated as



respectively. But if the anions are $[\mathrm{CO_3}]$ and $[\mathrm{NO_3}]$ with a similar arrangement of oxygens round the central atom, then the rhombohedral structure of these two compounds becomes explicable in terms of isomorphism. These ideas were developed by T. V. Barker (J.C.S. 1912, **101**, 2484), who showed that the following substances were members of isomorphous series : K_2SO_4, K_2BeF_4, and $(NMe_4)_2HgCl_4$ (orthorhombic), $KClO_4$, $BaSO_4$, and KBF_4 (orthorhombic), xenotime YPO_4, zircon $ZrSiO_4$, and cassiterite Sn_2O_4 (tetragonal),

$$Cu[TiF_6]4H_2O\ ;\ Cu[NbOF_5]4H_2O$$

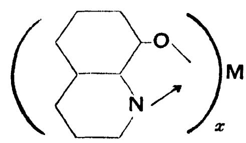
and $CuWO_2F_4,4H_2O$ (monoclinic). The double salt $K_2BeF_4,Al_2(SO_4)_3,24H_2O$ crystallises in cubic octahedra and is a true alum, as is also $K_2ZnCl_4,Al_2(SO_4)_3,24H_2O$ (W. R. C. Curjel, Nature, 1929, **123**, 206). In these substances the compounds $K_2[BF_4]$ and $K_2[ZnCl_4]$ are isomorphously equivalent to $K_2[SO_4]$.

Analytical Reagents.—The separation of copper from cadmium and of cobalt from nickel in qualitative analysis is based on the difference in stability of two pairs of double cyanides ; (1) hydrogen sulphide decomposes the cadmicyanide, $K_2[Cd(CN)_4]$, but not the cuprocyanide, $K_3[Cu(CN)_4]$; (2) hypochlorites or hypobromites decompose the nickelocyanide

$$Na_2[Ni(CN)_4]$$

but not the cobalticyanide $Na_3[Co(CN)_6]$. The quantitative estimation of nickel is facilitated by the use of its insoluble complexes with dimethylglyoxime, α-benzildioxime, or dicyanodiamidine. β-Naphthoquinoneoxime oneoxime dyes) gives a sparingly soluble cobalti-complex used in separating this metal from nickel. (*see* Chemical Analysis, vol. II, p. 612*c*).

Nitroso-β-phenylhydroxylamine (cupferron) furnishes insoluble red and white complexes with ferric and cupric salts respectively. The compound 8-hydroxyquinoline (oxine) has proved a useful analytical reagent for many metallic ions, since it yields insoluble products of the type indicated by the following general formula :

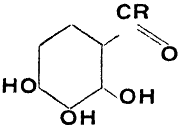


$x=2$, 3, or 4

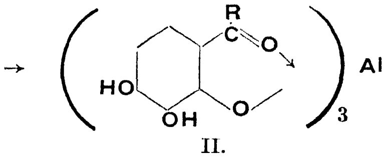
The reddish-violet colorations obtained by the action of alkaline copper solutions on biuret are complex salts $[(C_2O_2N_3H_2)_2Cu]K_2,4H_2O$ or $[C_2O_2N_3H_2Cu]K,3H_2O$, in which this iminodiamide is reacting in its monoenolic form $HN:C(OH)\cdot NH\cdot CO\cdot NH_2$.

Mordant Dyes.—Included within the two main categories of mordant and acid mordant dyes are many substances of very varied chemical structure, but these otherwise diverse compounds have one feature in common, a chelate group capable of entering into co-ordination with the metallic mordants generally employed in dyeing. The coloured effects produced on mordanted fibres are internal metallic complexes (insoluble lakes) arising from this combination of dye and mordant.

In many cases the dyes themselves have little or no colour. Alizarin yellow A and C are respectively benzoyl- and acetyl-pyrogallol (I), which, although but faintly coloured, furnish yellow aluminium lakes (II) :



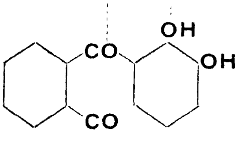
I.



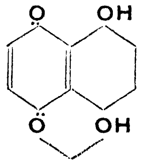
II.

The quinoneoxime dyes are also simple examples of pale yellow to brown mordant or adjective dyes (chelate group $HON:\underset{|}{C}—\underset{|}{C}=O$) which furnish green and dark brown lakes on wool mordanted with iron and chromium respectively.

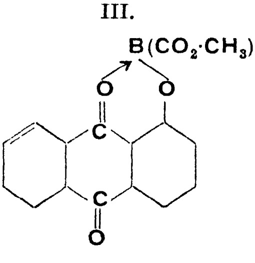
Alizarin (*q.v.*) and naphthazarin (alizarin black) supply further typical examples of such mordant dyes. The former (III) possesses 1 chelate group $CO\cdot\underset{|}{C}—\underset{|}{C}\cdot OH$, and the latter (IV) contains 2. When the hydrogens of the chelate groups are replaced by an appropriate metal (aluminium, iron, chromium, etc.) a coloured lake is produced.



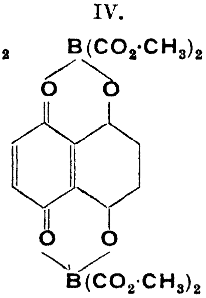
III.



IV.



V.



VI.

Treatment of III with pyroboric acetate reveals the presence of 1 chelate group (V), whereas with (IV) this reagent gives rise to a diboric ester containing 2 chelate groups (VI). Accordingly the quinone (IV) must be 5:8-dihydroxy-1:4-naphthaquinone and not the 5:6-dihydroxy analogue as formerly supposed (Dimroth and Ruck, Annalen, 1925, **446**, 123.

An azo-group often becomes implicated in the chelate complex, as in the case of many hydroxyazo- and dihydroxyazo- dyes. Such colouring matters are substantive dyes on wool or silk but their tinctorial effect is changed very considerably when the dye is converted into its lakes with suitable mordants. Eriochrome red B and Palatine chrome black 6B are examples of dihydroxyazo-dyes having chelate groups which give rise to deep red and black chromic complexes. In other instances the lake-producing chelate group is developed from the dye by oxidation, as when the dyed fabric is developed with chromic acid. Diamond black PV, Carmoisin WS, and the chromotropes are typical examples of such dyes (J. Soc. Dyers and Col. 1921, **37**, 43 ; 1925, **41**, 233). When these dihydroxyazo-dyes contain sulphonic groups it becomes possible to produce a soluble lake from dye and metallic mordant. These soluble lakes which already contain the inner metallic complexes can be applied substantively to animal fibres and have the further advantage that they may be used in metallic vessels, since the lake is far less affected than the dye by the metal of the container. A group of these soluble lakes is sold under the generic name of *neolan* dyes.

The natural mordant dyes such as cochineal, lac, logwood and the redwoods also contain chelate groups capable of co-ordinating with metallic mordants, and it is to the presence of such chelate groups (generally of the ortho-hydroxyketone type) that they owe their tinctorial properties.

Representative Minerals.—The chemical constitutions of many mineral species are most readily explicable in terms of co-ordination. The apatite group is a notable example, and it contains the following series : chloroapatite, $[Ca3\{Ca_3(PO_4)_2\}]Cl_2$, pyromorphite,

$$[Pb3\{Pb_3(PO_4)_2\}]Cl_2,$$

mimetite, $[Pb3\{Pb_3(AsO_4)_2\}]Cl_2$, vanadinite, $[Pb3\{Pb_3(VO_4)_2\}]Cl_2$.

The spinels having the general formula $R_2^{III}[R^{II}O_4]$ also form a noteworthy group of isomorphous minerals, including the following species: spinel, $Al_2[MgO_4]$, hercynite, $Al_2[FeO_4]$, chromite, $Cr_2[FeO_4]$, magnesioferrite, $Fe_2[MgO_4]$, gahnite, $Al_2[ZnO_4]$, and magnetite, $Fe_2[FeO_4]$. The naturally occurring silicates are also most readily explicable in terms of the co-ordination theory. In these minerals silicon has a co-ordination number of 4 as, for example, in the ion $[SiO_4]$.

Among copper minerals are the well-known atacamite

$$[Cu3\{Cu(OH)_2\}]Cl_2$$

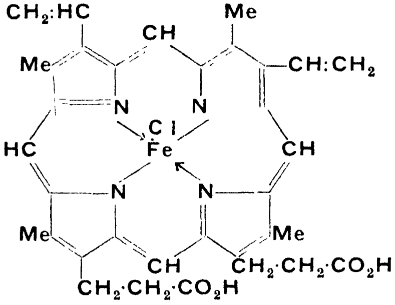
and the corresponding sulphate, brochantite, $[Cu3\{Cu(OH)_2\}]SO_4$. Contrary to an opinion which has prevailed for a century the green patina developing on copper roofs is not basic copper carbonate but basic copper sulphate, $[Cu\,x\{Cu(OH)_2\}]SO_4$, in which x varies from 1 to 3. In an artificial patina produced electrolytically, $x=1$, whereas in the natural patinas produced by exposure of more than 70 years x approximates closely to 3, so that the corrosion product is a co-ordination compound identical in composition with brochantite (Vernon and Whitby, J. Inst. Metals, 1930, **44**, 2, 389).

Substances of Physiological Significance.—The fluorine in the enamel of teeth is present in the form of fluorapatite, $[Ca3\{Ca_3(PO_4)_2\}]F_2$ (G. Shearer). The mineral portion of the bones of vertebrates consists mainly of carbonato-apatite, $[Ca\{(PO_4)_2Ca_3\}]CO_3$, and hydroxy-apatite, $[Ca\{(PO_4)_2Ca_3\}](OH)_2$ (Bassett, J.C.S. 1917, **111**, 636 ; Hendricks, Jefferson, and Mosley, Z. Krist. 1932, **81**, 382), whereas the bone ash from fish and mammals contains as main constituent the complex phosphate

$$[Ca6\{Ca_3(PO_4)_2\}](OH)_2$$

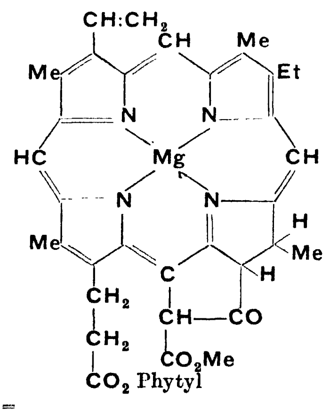
(Morgulis, J. Biol. Chem. 1931, **93**, 455).

An important co-ordination compound of physiological significance in the animal kingdom is hæmin (I), the essential ferruginous colouring matter of blood. Closely allied to this pigment is hæmocyanine, the blood colouring matter of crustaceans and molluscs, but in this compound copper replaces iron. Another copper pigment of similar type is turacin, a reddish-purple product present in the feathers of the touraco.



I.

In the vegetable world, the chief co-ordinated compound is chlorophyll, the green colouring-matter of plants. Two forms, α and β, have been recognised, and the structure of the former variety is indicated by II. The β form contains an aldehyde group replacing a methyl group, but both forms contain the 4- co-ordinated magnesium atom.



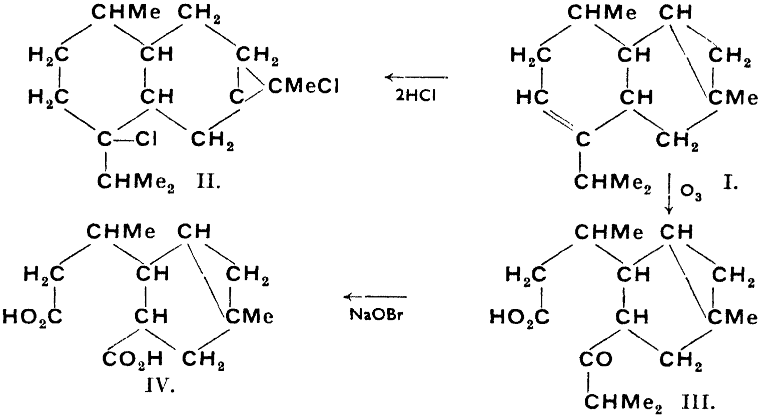
Phytyl = $Me_2CH{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CMe{:}CH{\cdot}CH_2$.

II.

References.—“Inorganic Chemistry, A Survey of Modern Developments,” by Sir Gilbert Morgan and F. H. Burstall, Heffer and Sons, Cambridge, 1936; “The Electronic Theory of Valency,” by N. V. Sidgwick, Oxford University Press, 1927; “Annual Reports of the Chemical Society,” 1930–1936.

G. T. M. and F. H. B.

COPAENE. The lævorotatory sesquiterpene hydrocarbon, *copaene*, $C_{15}H_{24}$, b.p. 119–120°/10 mm., d^{15} 0·9077, n_D 1·48943, $[\alpha]_D$ −13·21°, occurs in African Copaiba oil (from *Oxystigma Mannii*) (Schimmel's Report, 1914, April, p. 48) and in oil of supa, Henderson, McNab and Robertson assigned to it the structure (I) (J.C.S. 1926, 3077). this differs from that of Semmler and Stenzel (Ber. 1914, **47**, 2555) hydrogen chloride as regards the bridge. On treatment with it yields *cadinene dihydro-chloride* (II) whilst on oxidation with ozone or potassium permanganate it gives a monobasic ketonic acid, *copaene ketonic acid*, $C_{15}H_{24}O_3$ (III), (*semicarbazone*, m.p. 221°), which on further oxidation with sodium hypobromite yields a dibasic acid *copaene dicarboxylic acid*, $C_{12}H_{18}O_4$ (IV).



Apart from cadinene dihydrochloride no crystalline derivatives have been prepared from copaene.

J. L. S.

COPAIBA. Copaiba, or Balsam of Copaiba, is the oleo-resin obtained from various species of *Copaifera*, of which the most important is *C. Langsdorfii*. The oleo-resin is secreted in schizogenous ducts which eventually become lysogenous cavities in the trees, and these are opened by boring to allow the secretion to flow out. Copaiba is a thick, viscous liquid of a yellow to brown colour, often fluorescent. In commerce the balsam is sold on a description which indicates the place from which it is exported and which to a considerable extent covers the district in which it has been collected and, therefore, within reasonable limits, the species from which it has been obtained. The principal areas of its production are in Brazil and the northern portion of South America.

The best known varieties are Maranham, Maracaibo and Pará. The principal differences between the various balsams are in the proportions of essential oil and resin. Its use is entirely confined to medicine, and the standards of the 1932 edition of the “British Pharmacopœia” are as follows. Its specific gravity should be from 0·960 to 0·995, and the acid value of the residue obtained by drying in a water bath should be from 120 to 160. The optical rotation of the essential oil obtained by distillation by steam or under reduced presence should be from −7° to −35°. The resin obtained by drying on a water bath should be not less than 50% and not more than 65%.

At present copaiba is seldom adulterated, but if so, the principal adulterants are *gurjun* balsam and the so-called African copaiba.

Essential oil of copaiba (*q.v.*) is used to some extent in medicine, as is also the resin. For an exhaustive examination of a sample it is necessary to separate the essential oil and the resin and examine each separately. The essential oil is best distilled in a current of steam to avoid decomposition, which takes place even when the balsam is distilled *in vacuo*. The table at the top of p. 338 will show the figures for a number of typical authentic samples, but slight variations may be expected in a substance derived from several species under varied conditions. These values are merely typical, variations from them may be expected, and definite limits cannot be given.

For the detection of gurjun balsam oil, the determination of the optical rotation of the essential oil is important. Gurjun oil has a rotation which is rarely below −70° and often reaches −130°, so that a higher rotation than −35° in the essential oil renders a sample very suspicious. If 3 or 4 drops of the essential oil are dissolved in 3 c.c. of glacial acetic acid and the mixture is carefully poured on to the surface of concentrated sulphuric acid, a dark violet colour is developed in the acetic acid solution if 5% of gurjun oil be present.

The resin of copaiba consists for the most part of bodies of an acid nature. According to Schweitzer (Pogg. Ann. 1829, **17**, 784; 1831, **21**, 172) one principal constituent is a crystalline acid melting at 131°, to which the name *copaivic acid* was assigned. Its formula is given as

	Maranham.	Maracaibo.	Cartagena.	Pará.	Bahia.
Sp.gr. of balsam at 15·5°	0·990	0·980–0·995	0·950–0·970	0·920	0·975
Acid value of balsam. .	70–80	85–90	60–80	30–55	80
Refractive index of balsam (20°)	1·5120	1·515	1·510	1·508	1·506
Essential oil % . . .	40–50	45–48	42	75	44
Sp.gr. of oil at 15·5° . .	0·900	0·900	0·904	0·900	0·905
Refractive index of oil at 20°	1·4980	1·4980	1·4960	1·498	1·495
Optical rotation of oil at 20°	−18°	−10°	−20°	−25°	−18°
Acid value of resin . .	135	80–90	130	70	75
Ester value of resin . .	38	50	45	85	75

$C_{20}H_{30}O_2$. Numerous other acids have been described, but as little other than combustion results and empirical formulæ have been quoted, it is not necessary to reproduce them here (*see* Arch. Pharm. 1901, **239**, 548).

According to Freise (Perf. and Essent. Oil Rec. 1934, **25**, 218) there are 15 species of *Copaifera* to be found in Brazil. He has examined 8 samples from different species, and gives the following as their characters :

Species of *Copaifera*	*reticulata*	*guyanensis*	*multijuga*	*officinalis*	*Martii*, v. *rigida*	*coriacea*	*Martii*	*glycycarpa*
Place of collection . .	Tapajóz	Rio Negro	Tapajóz	Rio Negro	Pará	Bahia	Santarem	Maués (Amaz.)
Sp.gr. (15°/4°)	0·94–1·004	0·93–0·975	0·92–0·955	0·95–0·998	0·93–0·96	0·925–0·965	0·888–0·912	0·958–0·985
Optical rotation (100 mm. tube, at 20°) .	−35° 40′/ −37° 10′	−28° 30′	Not determined		−14° 45′/ −19° 20′	−22° 30′/ −28° 15′	Not determined.	
Acid no. . .	74–81	68–71	81–86	64–68	72–77	58–82	48–67	65–82
Saponification no. .	89–91	92	77–82	62–70	68–88	Not. det.	44–62	72–77
Solubility in 90% alcohol: vols., minimum .	6	5·5	6	4·5	12	10	5·5	12
Essential oil, % . . .	26–31·5	28·5	48·5–55	55–58	60–63	55–62·5	38–52	32–38·5
Sp.gr. of oil, (15°/4°) .	0·935/0·938	0·910/0·912	0·895	0·915/0·918	0·926/0·929	0·911/0·914	0·922/0·928	0·925/0·945

See also Balsam of copaiba, "Allen's Commercial Organic Analysis," 5th ed., Vol. IV, p. 307; Deussen and Eger (Chem.-Ztg. 1912, **36**, 561) ; Cocking (Chem. and Druggist, 1910, **77**, 119); and von Soden (Chem.-Ztg. 1909, **33**, 428).

It will be convenient to describe here the so-called African copaiba. This body is also known as *Illurin balsam*. Its botanical origin is uncertain. It has been ascribed to *Oxystigma Mannii* Harms, but is more probably the product of *Daniellia thurifera*. It closely resembles true copaiba in characters, the principal physical difference being that its essential oil is dextrorotatory. The characters of the balsam are as follows :

Specific gravity . . .	0·985–0·998
Acid value	55–60
Ester value	8–10

Illuric acid, $C_{20}H_{28}O_2$, melting at 128°, is stated to be the chief of the resin acids (Tschirch and Keto, Arch. Pharm. 1901, **239**, 548).

E. J. P.

COPAIBA, ESSENTIAL OIL OF.—The oil distilled from the oleo-resin or balsam of copaiba derived from various species of *Copaifera* (Fam. Leguminosæ), which are large trees found chiefly in Brazil, Venezuela, Guiana and Colombia. The oleo-resin is a secretion which is obtained by boring the tree and collecting the exudation. It is imported from Maranham, Maracaibo, Pará, Cartagena, and Cayenne. The Pará variety yields 65–80% of oil, the other varieties 35–55%.

Composition.—This oil consists mainly of the sesquiterpenes, β-caryophyllene and cadinene.

Characters.—It is a colourless or pale yellow oil, sp.gr. 0·895–0·908, opt. rot. −7° to −35°, ref. ind. 1·495–1·500. A solution of 1 ml. of oil in 5 ml. of glacial acetic acid should not develop more than a faint reddish or purple coloration on the addition of 4 drops of nitric acid (absence of gurjun balsam). When distilled under reduced pressure the first 10% fraction has an optical rotation lower than that of the original oil (absence of oil of African copaiba). The oil is used in medicine as a urinary antiseptic.

C. T. B.

COPAL.—This varnish resin is, from a commercial point of view, of very great importance. It will be convenient to deal with its numerous varieties, from a geographical point of view. The principal of the copals are as follows:

(1) East African copals.
(2) West African copals.
(3) Kauri gum or New Zealand copal.
(4) East Indian and Manila copals.
(5) South American copals.

(1) The trees yielding East African copal (Zanzibar, Lindi and Tanganyika) are *Trachylobium verrucosum* (Fam. Legamimosæ), *Hymenæa verrucosa* (Madagascar) = *Trachylobium verrucosum* and *Copaifera conjugata* Milne-Redhead (Inhambane).

The resin ducts are near the surface and no injury to the tree is necessary. Native collectors recognise three varieties of copal : (*a*) that obtained direct from the trees ; (*b*) that which has dropped from still growing trees and collects in the soil, where it has hardened, known as "semi-fossil" copal ; and (*c*) that found in the soil, which has been dropped from trees no longer existing, known as fossil resin. Some of the fossil resin has characteristic rough markings, and is known as "goose skin" copal. This is probably due to uneven contraction of the various layers during drying.

The following analyses of East African copal—known generally as Zanzibar, although the greater part is produced on the mainland—are due to the Belgian Ministry of Colonies (Revue générale de la Colonie belge, 1921, 552).

	Sp. gr.	Moisture. %	Ash. %	% soluble in alcohol.	Acid value.	Sap. value.
1	1·062	0·81	0·04	53·16	83·1	83·1
2	1·071	0·87	0·04	57·88	86·7	89·5
3	1·062	0·80	0·04	48·20	87·6	89·1
4	1·064	1·15	0·05	52·22	100·7	100·7
5	1·067	0·89	0·02	54·53	100·1	100·1
6	1·061	0·81	0·06	51·72	95·9	96·0
7	1·074	0·66	0·08	93·74	153·9	165·1
8	1·053	0·59	0·04	93·18	166·9	166·9
9	1·057	0·58	0·01	81·39	142·7	151·1

Similar analyses of Madagascar copal (*l.c.*) gave the following results :

	Sp. gr.	Moisture. %	Ash. %	% soluble in alcohol.	Acid value.	Sap. value.
1	1·062	0·52	0·014	76·05	140 3	155·7
2	1·060	1·09	0·40	57 31	111·08	140·3
3	1·052	1·05	0·27	49·28	100·8	111·8

The constituents of Zanzibar copal are not known with any degree of certainty. Resenes and acids with very high molecular weights have been quoted, but until a series of well-defined derivatives has been prepared, the individuality of these bodies cannot be relied on. Reference may be made to the papers of Tschirch and his fellow workers (Arch. Pharm. 1896, **234**, 552 ; 1897, **235**, 92 ; 1901, **239**, 145, 298 ; 1902, **240**, 202, 478 ; 1908, **246**, 293).

(2) Of West African copals, Congo copal is by far the most important. The greater part of the exports consists of fossil resin. Sierra Leone copal is obtained from living trees. Various other copals or so-called copals are produced in other West African districts. The copal from the Belgian Congo is derived chiefly from *Copaifera Demeusei* Harms, and to a smaller extent from other *Copaifera* species. A large number of samples have been examined by the Belgian Ministry of Colonies, which have been collected in numerous districts. These samples gave results within the following limits :

Specific gravity . . .	1·033–1·065
Moisture %	0·26–1·00
Ash %.	0·017–0·06
Soluble in alcohol %. .	38·82–70·53
Acid value	85·4–143·7
Saponification value .	91·1–149·5

For Tschirch's views on the composition of Congo copal, *see* Tschirch and Engel, Arch. Pharm. 1908, **246**, 293.

Hellinckx gives figures for Congo copal which are of value, since the samples are all graded as to colour :

No.	Grade.	Appearance.	Melting-point °C.		Sp.gr.	Acid value.	Sapon. value.	Iodine value.
			Lower.	Upper.				
1	White	Transparent white . . .	120	178	1·0509	100	120	104
2	,,	Opaque white	—	—	1·0585	130	136	82
3	,,	Yellowish white, transparent	110	160	1·0482	117	132	73
4	,,	Pinkish white, transparent .	110	160	1·0459	104	130	90
5	,,	So-called "black" type .	108	147	—	—	—	—
6	Dark	Dark brown, much impurity	135	185	—	—	—	—
7	,,	Dark brown, some impurity	132	185	—	98	128	70
8	,,	Pale brown, transparent .	132	183	1·0498	114	150	74
9	,,	Brown, transparent . . .	135	190	1·0633	114	150	54
10	Amber	Ivorine	90	135	—	84	120	59
11	,,	Pale brown, white striations	126	160	1·0486	85	150	96
12	,,	Brownish, opaque . . .	130	167	—	90	130	14
13	,,	Brown, chalky appearance .	125	195	—	79	121	110
14	,,	Yellow opaque	95	145	1·0550	42	59	72

It will be seen that the analytical examination of copal must be regarded as quite subsidiary to the expert knowledge gained by those accustomed to handle specimens of known origin.

(3) Kauri gum or New Zealand copal is the product of *Agathis australis* (Fam. Araucariaceæ), the fossil "gum" being dug from the soil. The tree is said to live for over 3,000 years.

Kauri "gum" varies greatly in quality, as some is found in fine, clear, bold pieces, some as small fragments, and some adherent to old tree stumps, from which it has to be extracted.

This resin has the following characters :

Moisture %	2–5
Ash %	0–0·2
Acid value	60–80
Saponification value . .	84–130
Insoluble in $CHCl_3$, % .	2–20
Iodine value	100–125

Tschirch and his fellow workers have, as with most of the copals, given formulæ for various acids isolated from this resin, but the most recent work on the subject is that of Ruzicka and Hosking (Annalen, 1929, **469**, 147 ; Helv. Chim. Acta, 1930, **13**, 1402 ; *ibid.* 1931, **14**, 203. They isolated a crystalline acid, $C_{20}H_{30}O_{40}$, which they termed agathic-bicarboxylic acid (*q.v.*) It is present in both New Zealand and Manila copals. An ether-soluble amorphous resin acid from Manila copal on dehydrogenation with selenium gave 1 : 2 : 5-trimethylnaphthalene, a hydrocarbon, $C_{17}H_2$, and retene, whilst agathic acid yielded pimanthrene but no retene.

(4) The East Indian and Manila copals, which include the copals from the islands of the South Pacific from Sumatra and the Malay Peninsula on the west to Celebes and the Philippine Islands on the east, are derived mostly from the living tree *Agathis alba.* These copals have the following characters :

Acid value (of pure resin) . . .	120–150
Saponification value (of pure resin)	165–190
Iodine value	90–120

For the older views as to chemical composition, *see* Tschirch and Koch (Arch. Pharm. 1902, **240**, (3), 202) and Richmond (Philippine J. Sci. 1910, **5**, 177).

Ruzicka, Steiger and Schinz (Helv. Chim. Acta, 1926, **9**, 962) have examined Manila copal and found it to consist of 80% of acids as follows :

(i) A monobasic acid, $C_{15}H_{24}O_2$ or $C_{16}H_{26}O_2$

(ii) A dibasic acid, $C_{23}H_{34}O_4$, apparently identical with Richmond's acid, $C_{23}H_{34}O_4$.

(iii) A dibasic acid, $C_{40}H_{60}O_4$.

(5) The South American copals are probably derived from species of *Hymenæa,* but are not of great commercial importance.

In general properties the copals vary in colour from white to yellow, red, brown and brownish-black ; their softening and melting-points and their specific gravities also vary. An excellent criterion of the value of copal is its hardness. Generally speaking the harder the copal the greater its value, but this does not always apply to kauri copal. The following table fairly represents the average hardness of copals taken in their order, with Zanzibar copal at the head of the list :

(1) Zanzibar.
(2) Mozambique.
(3) Lindi.
(4) Red Angola.
(5) Pebble Copal.
(6) Sierra Leone, old.
(7) Yellow Benguela.
(8) White Benguela.
(9) Cameroon.
(10) Congo.
(11) Manila.
(12) White Angola.
(13) Kauri.
(14) Sierra Leone, new.

Copal is partially soluble in many organic solvents ; for example, in alcohol, especially after it has been left to swell up in ether. But to convert copals into a completely soluble form it is necessary to heat them, sometimes even to the point of destructive distillation at 400°C., when the resin becomes soluble in turpentine or linseed oil.

Many analytical values have been published for copal in general. The following papers should be consulted : R. Williams (Chem. News, 1888, **58**, 224) ; Lippert and Reissiger (Z. angew. Chem. 1900, **13**, 1047) ; Schmidt and Erban (Z. angew. Chem. 1889, **1**, 35) ; Worstall (J. Amer. Chem. Soc. 1903, **25**, 860) ; Hellinckx (Dissertation, Louvain University, 1935).

Iodine Value.—The most full examination of the iodine value is that of Worstall (*l.c.*) and, for Congo copal, Hellinckx (*l.c.*). Worstall gives the following values based on the Hübl method :

<table>
<tr><th>Type.</th><th>Maximum.</th><th>Minimum.</th></tr>
<tr><td>Kauri . . . .</td><td>170</td><td>74</td></tr>
<tr><td>Manila . . . .</td><td>148</td><td>104</td></tr>
<tr><td>Pontianac . . . . .</td><td>142</td><td>119</td></tr>
<tr><td>Zanzibar . . . . . .</td><td>123</td><td>115</td></tr>
<tr><td>Mozambique . . . .</td><td colspan="2">136</td></tr>
<tr><td>Madagascar . . . . .</td><td colspan="2">126</td></tr>
<tr><td>West African . . . .</td><td>143</td><td>122</td></tr>
<tr><td>Sierra Leone . . . .</td><td>105</td><td>102</td></tr>
<tr><td>Brazilian . . . . .</td><td>134</td><td>123</td></tr>
</table>

E. J. P.

COPALIN. Highgate resin. A fossil resin found in the blue clay of Highgate Hill.

CO-PIGMENTS. The influence of tannin in increasing the blue tone of anthocyanin flower pigments when they are in solution was first observed by Willstätter and Zollinger (Annalen, 1916, 412, 212). The phenomenon was further studied by G. and R. Robinson (Biochem. J. 1931, **25**, 1687; 1932, **26**, 1647), who discovered the importance and significance of not only tannins but of other colourless substances in flower colour variation. They termed all these compounds which turn anthocyanins blue "co-pigments." Typical co-pigment effects are seen in magenta and rose-pink Chinese primulas as compared with red and salmon ones, and in the purple inner petals of the fuchsia.

A co-pigment effect is visible *in vitro* as well as *in vivo,* but is lost at boiling-point or on extraction with an immiscible solvent, such as amyl alcohol or ethyl acetate, and regained on cooling or on reprecipitation of the co-pigment into the aqueous layer.

These compounds are specific in their action and exist for all types of anthocyanins, but with a few outstanding exceptions pelargonidin derivatives, especially 3-biosides, are not found to be greatly affected by co-pigments. The chief natural co-pigments appear to be the tannins and anthoxanthin (flavone and flavonol) glycosides. Experimenting with synthetic compounds, G. and R. Robinson found that while 2-hydroxyxanthone, papaverine and quinaldine act as strong co-pigments on specific anthocyanins, 4-hydroxyxanthone, laudanosine and quinoline have very little action. They suggest that the phenomenon has little or nothing to do with salt formation, since it occurs in the presence of a large excess of mineral acid; but is evidently the result of the formation of weak additive complexes which are dissociated at an elevated temperature or by the action of solvents.

Co-pigments not only modify the colour of acid anthocyanin extracts, but they also have specific effects upon distribution numbers and upon the colour reactions with ferric chloride, sodium carbonate or sodium acetate.

Robinson, Robinson and Roberts (Biochem. J. 1934, **28**, 1712), using narcotine and papaverine as co-pigments for oenin and chrysanthemin, found that the extent of the depression of the normal distribution number (the partition value between amyl alcohol and aqueous acid) was correlated with the extent of the co-pigment effect. Papaverine was in both cases much more effective than narcotine. On plotting the log. curve for the distribution of oenin or chrysanthemin between amyl alcohol and water at various concentrations a slope of 1 instead of 2 was obtained when excess papaverine was present. Since it had already been deduced by Levy and Robinson (J.C.S. 1931, 2720) that in aqueous solution anthocyanins were associated as double molecules, while they were single in the bluer amyl alcohol layer, these results with co-pigmented extracts point to the breaking up of the double molecules by a combination between alkaloid and anthocyanin, thus giving the distribution and blueing effect compatible with single molecules. When compared over a large range of p_H values, co-pigmented anthocyanins are always found to be bluer than the normal pigment (*cf.* Buxton, J. Genetics, 1932).

The researches (Robinson *et al.*) upon the marked specificity of co-pigment action were followed by Lawrence's observations (Nature, 1932, **129**, 834) upon co-pigmentation in *Dahlia*, and upon the remarkable variation in the specific effects of various crude ivory anthoxanthin extracts upon a number of natural anthocyanins (*see* Scott-Moncrieff, J. Genetics, 1936, **32**, 117). The effect of these ivory pigments upon malvidin 3-monoglycoside was extreme; with cyanin the effect was strong but not so marked, while pelargonin was only slightly modified. Moreover, each anthocyanin was modified in a different degree by each of the anthoxanthin extracts.

Since the production of anthoxanthins and of anthocyanins is inversely correlated, a co-pigmented magenta or blue flower is necessarily paler in colour than the corresponding red or purple unco-pigmented variety (Lawrence and Scott-Moncrieff, J. Genetics, 1935, **30**, 155).

R. S.-M.

COPPER (Fr. *Cuivre*; Ger. *Kupfer*). Sym. Cu, at. wt. 63·57, at. no. 29, isotopes 63, 65.

Occurrence.—Copper occurs in the native state in many localities and is widely distributed as compounds of the metal, the following being the most important minerals from which it is extracted: *native copper*, sometimes associated with silver and bismuth; oxides, *cuprite* Cu_2O, *tenorite* or *melaconite* CuO; sulphides, *chalcopyrite* or *copper pyrites* Cu_2S,Fe_2S_3, *chalcocite* or *copper glance* Cu_2S, *covellite* CuS, *bornite* or *erubescite* Cu_5FeS_4; double sulphides with antimony or arsenic, *tetrahedrite* $4Cu_2S,Sb_2S_3$, *tennantite* $4Cu_2S,As_2S_3$, *famatinite* $3Cu_2S,Sb_2S_5$, *enargite* $3Cu_2S,As_2S_5$, *bournonite*,

$$3(PbCu_2)S,Sb_2S_3;$$

sulphate, *chalcanthite* or *copper vitriol* $CuSO_4,5H_2O$; carbonates, *malachite* $CuCO_3,Cu(OH)_2$, *azurite*, $2CuCO_3,Cu(OH)_2$; silicates, *chrysocolla* $CuO,SiO_2,2H_2O$, *dioptase* CuO,SiO_2,H_2O; chloride, *atacamite*,

$$CuCl_2,3Cu(OH)_2.$$

The importance of the several species of ores in the above list varies very much with the locality. Thus, while native copper occurs to a considerable extent in the Lake Superior district of North America and at Monte Catini, Italy, and is worked for the metal, and atacamite occurs and is worked at Los Remolinos and the Atacama Desert, South America, these minerals would in other localities be looked upon as rather rare, and as occurring only in the zone of weathering of copper lodes. So also in the case of malachite, this mineral, as an ore of copper, has been seldom worked except in small quantities in the upper and oxidised portions of some copper lodes, yet in the case of the once celebrated Burra Burra mine in South Australia and at Nishni-Tagilsk in Siberia it formed the bulk of the ore produced, and very large quantities have been obtained from these districts. The most remarkable deposit of malachite is that of the Katanga region of the Belgian Congo and the adjacent part of Northern Rhodesia; this is a most important field for copper and produced over a quarter of a million tons of the metal in 1936; the minerals are malachite, azurite, chrysocolla, melaconite, chalcocite, together with, at some mines, chalcopyrite and bornite; chalcopyrite and other sulphides are encountered at depth.

Chalcopyrite is the principal commercial source of copper and occurs in a number of ways, the most important of which are hydrothermal veins as in California, Montana, Arizona, Alaska, and Canada, pyrometasomatic deposits in which the chalcopyrite occurs with other sulphides at or near the contact between bodies of intrusive rock and limestone as Clifton-Morenci and Bisbee, Arizona; Bingham, Utah; Alaska, Canada, Australia, Japan, and Korea. Chalcopyrite associated with bornite occurs in the Kupferschiefer at Mansfeld, Germany, where the copper minerals occur as grains in a shale and are of sedimentary origin deposited at the same time as the shale.

The world's production of copper is about 1½ million tons per annum, of which the United States, Chili, and the Katanga area of the Belgian Congo and Rhodesia each produce about one-fifth. Copper ores frequently carry a low percentage of copper; thus some ores worked at a profit carry only 0·5% of the metal, and the average content is probably about 2·0%. The ore reserves of the Nchanga Consolidated Copper Mines of Northern Rhodesia are estimated at about 128 million tons having a copper content of 4·66%. The Nchanga West portion of this total is 41 million tons which includes 5½ million tons containing 17% copper. The importance of the Northern Rhodesia deposits can be realised from the fact that in 1936 the ore reserves were reported as 500 million tons, with an average content of 4·11% copper (Parker and Gray, Trans. Inst. Min. Met. 1936, **45**, 330).

EXTRACTION.

Generally speaking, in all copper ore deposits a certain amount of oxidised material is found in the portions near the surface, but as depth is attained and almost invariably at or about the level at which water is reached, the copper-bearing minerals change and the oxidised minerals give place to sulphide minerals, and these finally to chalcopyrite intimately mixed with varying proportions of pyrite. Chalcopyrite thus diluted down with pyrite, pyrotite, etc., forms the ore from which the greater proportion of the world's copper supply is derived, and the bulk of the material treated at smelting works generally. Such ore sometimes contains appreciable quantities of gold and silver. The silver is frequently carried by intermixed fahl ore, but also in many instances by the pyritic mixture in which distinct silver-bearing minerals are not observable. The ores as mined generally contain only small percentages of copper, frequently not more than 1%, and are submitted to some form of concentration, the most important being flotation processes by means of which a concentrate is obtained much richer in copper and more suitable for treatment and a tailing containing very little copper, which can be discarded.

The actual extraction of the metal and production of copper in the metallic state is carried out by one of two distinct types of process; one of these, by far the most important because of its very general application, treats the ore by smelting and is known as the dry method. The other—of only limited application—treats the material with solvents, thus obtaining the copper in solutions, from which it is recovered by suitable means, these processes are known as wet methods.

The main consideration which has to be taken into account in deciding whether a dry or a wet method is best for any given ore is the nature of the ore itself, but other considerations include the locality of the ore deposit, and this includes the availability of suitable fuel supplies, water supply, suitable labour, and other requirements.

Dry Methods.—These methods are suitable for ores in which the copper is present as sulphide, and the object of the first stage of the smelting process is to obtain the copper in a concentrated form in the first product of smelting. For this purpose the ore is smelted under oxidising conditions in such a way as to produce as the main product a "matte" or "regulus" which consists of cuprous sulphide, Cu_2S, and iron sulphide, FeS, in varying proportions, together with sulphides of certain other metals which may be present in the ore. Practically the whole of the copper present in the ore thus passes into the matte and a second product containing only traces of copper, slag, is also formed. The slag consists of the silica originally present in the ore, combined with oxide of iron formed by the oxidation of part of the iron sulphide present together with earthy bases also present or with lime added to the charge. The slag is thus mainly composed of iron silicate, and owing to its lower specific gravity separates easily from the matte and is removed to the slag dump.

Having thus concentrated the copper in the matte, the second stage of the process consists in the decomposition of this matte in such a manner as to eliminate the iron and sulphur and, as far as possible, other metallic elements which may be present and to yield the copper in the metallic state. For this purpose complete oxidation of the iron sulphide present and the combination of the oxide of iron formed with silica to form a slag is carried out, together with partial oxidation of the cuprous sulphide and subsequent reaction of copper sulphide and oxide yielding metallic copper. This is not sufficiently pure for the market as it may contain small quantities of impurities originally present in the ore and it may also contain gold and silver worth recovering. This impure copper is commonly known as blister copper, from the fact that large blisters are found on the surface of the pigs of copper, formed by the evolution of sulphur dioxide from the metal during its solidification.

The final process therefore consists in the refining of the copper produced as above, or in removing as far as practicable the small quantities of such elements as may still be present which would either injuriously affect the metal for manufacturing purposes or be of sufficient value to be worth separating.

The treatment of the ore involves, therefore, three distinct operations:

1. Smelting the ore with the production of matte and slag.
2. Treatment of the matte for the production of crude copper.
3. Refining the crude copper.

1. SMELTING THE ORE WITH THE PRODUCTION OF MATTE AND SLAG.—The object of this process being the concentration of the copper in the matte, the chief considerations kept in view are the production of a matte as rich in copper and a slag as poor in copper as is practically

and economically possible. The desired grade of matte for subsequent treatment having been decided upon, the smelter regulates this by suitably proportioning the sulphur in the charge to be treated so that there shall be sufficient to form Cu_2S with all the copper present and a further quantity to form FeS with some of the iron present so that the matte produced shall contain the required percentage of copper. From these considerations it will be seen that the factor which regulates the grade of the matte is the proportion of sulphur to copper present in the ore mixture to be smelted. When smelting purely pyritic ores or concentrates it frequently happens that the quantity of sulphur present is considerably in excess of requirements, and if smelted direct would result in a low grade of matte, so that the production of the most suitable grade necessitates the removal of this excess of sulphur by a preliminary operation known as " calcining " or more properly " roasting."

This process consists in subjecting the ore to a dull red heat under oxidising conditions so that the sulphur combines with oxygen derived from air admitted and in contact with the ore with the production of sulphur dioxide, which is generally used for the manufacture of sulphuric acid, while oxide of iron and oxide of copper to some extent are formed at the same time.

The method of carrying out this roasting process depends upon the nature of the ore and also upon the locality; thus it may be roasted:

(*a*) In the rough or lump form—in pieces from ¾-in. cube upwards; or

(*b*) In the finely divided state or as concentrates obtained by preliminary mechanical washing of the ore or by flotation.

Under (*a*): Copper ores were formerly roasted in heaps in the open air by starting the combustion by means of wood, the combustion being maintained by the sulphur in the ore. It is evident that there must be objections to this method owing to the contamination of the atmosphere with sulphur dioxide, and there are few localities where such a method would now be tolerated. As an improvement on heap roasting, stalls and kilns have previously also been used; these consisted of series of chambers built back to back, suitable flues being arranged to carry the fumes to a chimney stack. An improvement on these methods consisted of the use of " burners " or closed chambers similar to those used for burning pyrites in sulphuric acid works, the sulphur dioxide being used for the manufacture of sulphuric acid.

Under (*b*): Finely divided copper ores were formerly roasted in long-bedded reverberatory furnaces to which a firebox was attached at one end and an exit for the gases at the other end. The ore was dropped from a hopper through an opening in the roof on to the bed at the flue end of the furnace, where it was spread out by suitable tools worked by hand. The conditions in the furnace were intensly oxidising and the charge was slowly moved from the flue end to the firebox end by the workmen, losing sulphur on its way, and finally being discharged through openings in the bed into vaults or chambers placed below. The labour required on these furnaces was very heavy and the output small, so that they have now been displaced by other methods of roasting, including those in which the ore is stirred, moved forward, and discharged by mechanical means operated by power.

Several forms of straight-hearth mechanical furnaces have been used similar in principle to the hand calciner. For example, one such calciner consists of a flat bed, 100 ft. or more in length, covered with an arch. At the cool end is the inlet for the ore and at the opposite end is the outlet. At the hot end also, but on the side of the furnace, is a firebox with its inlet to the furnace constructed in the roof of the latter. Other similar fireboxes are placed along the length of the furnace, and at the cool end is the flue for carrying off the gases. A channel is constructed in the side walls of the furnace in which rails are laid and suitable carriages with wheels resting on the rails stretch across the furnace, to these ploughs are attached which, passing through the furnace, turn over and mix the ore and at the same time carry it forward. The carriages and ploughs are moved by a pair of endless chains which cause them to travel through the furnace in one direction and to return in the other direction under the furnace bed. Each time the carriage enters the furnace it takes in with it a portion of ore or concentrate to be roasted and each time it leaves the furnace it carries out a similar portion of roasted product.

The McDougall furnace (Fig. 1) is typical of the class of roaster largely used at the present time. This consists of a series of flat, circular, superimposed firebrick hearths enclosed in a brick-lined cylinder of steel plate. An iron shaft passes centrally up the cylinder through openings in the several hearths and is caused to revolve by suitable gearing attached to one end. This shaft is cooled by water or air. Arms are attached to this shaft above each bed. These arms extend from the shaft to the periphery of the circular beds and have attached to them a series of ploughs set at a slight angle to the arm. The ore is fed from a hopper on to the top bed near the outside and as the arms revolve they turn the ore over and gradually move it from the outside to the centre of the bed. At this point is an opening through which the ore falls on to the second bed. On this bed the ploughs are so set on the arms that the ore travels in the reverse direction and is drawn to the outside of the bed. Here it discharges on to the third bed and so on until it passes out at the bottom of the furnace. Arrangements are made for the charging of this hot roasted material into reverberatory furnaces with as little fall in temperature as possible, leading to economy in fuel. The openings through which the ore falls from one bed to the other serve as flues through which the gases pass upwards through the furnace, finally escaping through a flue above the top bed to the sulphuric acid plant. Attached to the lowest bed is a firebox by which the furnace is heated up in order to start the roasting; after once being started, little or no fuel is required, as the oxidation of the ore provides sufficient heat throughout the apparatus; a partial removal of sulphur is all that is required.

Another method of removing the excess sulphur which has been used is known as "pot roasting" or "blast roasting." This method has been applied to concentrates and fines and, while it eliminates the sulphur, the heat attained is at the same time sufficiently intense to cause the ore to partially melt or sinter together, forming a mass which requires to be broken up but is suitable for blast-furnace treatment.

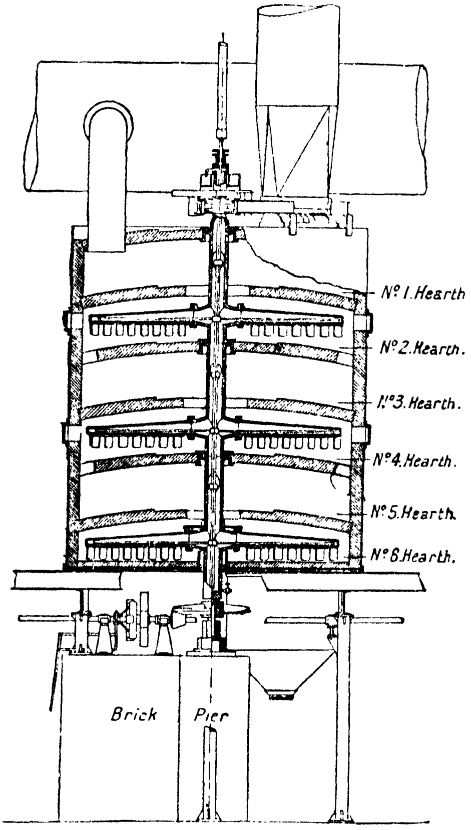


FIG. 1.

The process is carried out in a similar manner to that used in the treatment of lead and zinc ores but is little used in the metallurgy of copper.

After the sulphur in the ore mixture has been reduced to the requisite amount it is ready to be smelted. For this operation one of two distinctly different types of furnace is used. These are: (i) blast furnace; (ii) reverberatory furnace.

The choice between these methods of smelting depends on a variety of circumstances, all of which must have proper consideration, but the following are the chief points, viz.: if the ore to be smelted is in the state of concentrates as most of the material is at the present time owing to the development of concentrating methods and especially of flotation processes, it is generally unsuitable for blast furnace treatment, while it is eminently suitable for the reverberatory furnace. On the other hand, rough ore is unsuitable for reverberatory furnace smelting, and for this blast furnaces are used. Certain ores which carry gold and silver in the gangue minerals and ores which contain both sulphide and oxidised minerals of copper are best treated in blast furnaces. During the smelting of the former, the precious metals will pass into the matte formed and will be carried into the metallic copper obtained, from which they are easily recovered during electrolytic refining.

(i) *Blast Furnace Smelting.*—The furnace used is constructed with water-cooled walls of steel plate, each section of which is termed a jacket and is generally rectangular in shape. As the working of this type of furnace is dependent upon an air blast projected into the interior, the width of the furnace is limited by the strength of the blast which is required to penetrate the charge from the sides to the centre of the furnace, while the length of the furnace is only limited by the capacity required. The increase in length is obtained by clamping together two or more of the jackets on each side, thus extending the longer axis of the furnace.

The jackets stand on a thick cast-iron plate carried on iron supports. In some cases, as in Fig. 2, these jackets are only used in the lower part of the furnace, the upper part being constructed of brick, but the brickwork is now generally replaced with a second tier of jackets reaching up to the feed floor. Above the feed floor the furnace is continued in the form of a covered-in brick chamber with lifting doors for charging and an outlet for the waste gases. The charge consists of a proper mixture of ore—either raw, raw and calcined, or partially calcined—flux, either limestone or silicious material, and the necessary amount of coke required to form a suitable smelting mixture. On the lower floor the furnace is provided with spouts through which the molten products of the furnace flow. The side jackets of the furnace are provided with circular openings forming a horizontal line of openings on each side of the furnace through which the tuyères pass for the admission of the blast. The blast at a suitable pressure is generated by a blowing engine and a plentiful supply of water is circulated through all the jackets, the overflow pipes carrying away the hot water.

The products of the smelting operation carried out in this furnace flow out through a spout into the settler. This settler consists of a tank, constructed of steel plates lined with refractory material placed in position under the spout. It may be 10 ft. or more in diameter and is provided with a slag spout near the top and a tap hole near the bottom. In this vessel a separation of the matte and slag takes place; the matte having the higher specific gravity falls to the bottom and the lighter slag rises to the top, whence it overflows through the slag notch into suitable pots provided for its removal to the slag dump. From time to time the matte is tapped off through the tap hole at the bottom of the settler for further treatment. The working of this type of furnace proceeds continuously, fresh ore mixture and coke being charged at short intervals while a constant flow of matte and slag passes out through the spout into the settler.

Pyritic Smelting.—This method of working in the blast furnace secures in one operation that which in the preceding description is attained in two processes carried out in separate furnaces. In pyritic smelting the high temperature necessary to carry on the smelting is derived from the oxidation of the sulphur and iron (chiefly the latter) contained in the ore itself. While this method of working without coke as a fuel is of the highest importance from an economical point of view, it is of limited application owing to the fact that comparatively few mines produce ore which, as regards its physical and chemical constitution, is suitable for this method of treatment. In working the process it is found advantageous to use from 1 to 3% coke instead of the 10 to 12% used in the ordinary blast-furnace method of smelting roasted ore. A small amount of coke used alters the process to a partial pyritic smelting, and is found to be desirable in order to keep the charge open.

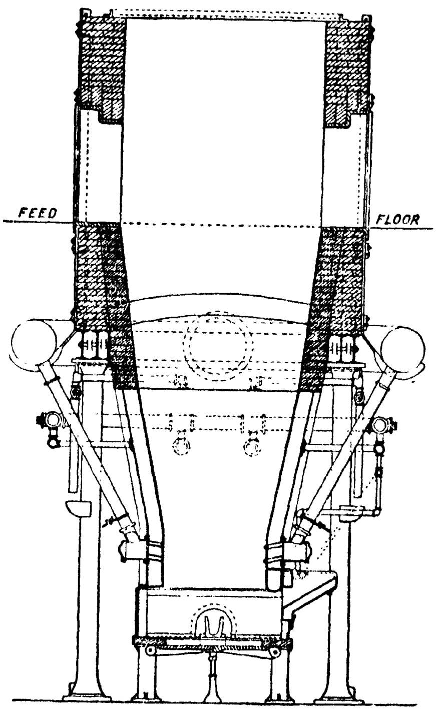


Fig. 2.

In the Mt. Lyell smelter practice the flotation concentrate carrying 26% copper and 12% moisture is charged direct to the blast furnace without drying, roasting, or sintering. The blast-furnace treatment of this fine material has necessitated the introduction of an efficient dust-collecting system in which 30 tons of dust per day, containing 25% copper, are obtained. This dust is incorporated with the concentrate pulp prior to filtration, and so is returned to the blast furnace (J. N. Greenwood, Proc. Austral. Inst. Min. Met. 1936, No. 103, 225).

(ii) *Reverberatory-Furnace Smelting.*—The furnace used in this process is essentially different both in construction and in method of working from the blast furnace. Instead of the fuel—coke—being burnt in contact with the materials to be smelted and the combustion being carried on by means of an air blast, the material to be smelted occupies one compartment of the furnace while the fuel, if lump coal be used, is burnt in another. The draught required for the combustion of the fuel is quite moderate and is obtained by a chimney of suitable height and area. The use of lump coal firing has given way almost entirely to the use of pulverised coal or oil fuel which is introduced through suitable burners. The working bed of the furnace in plan is a parallelogram. At one end and separated from it by a low partition is the firebox or space for necessary burners. At the opposite end is the outlet flue connecting with the chimney. A brick arch extends from the firebox end to the flue and covers the furnace from side wall to side wall. The side walls of the furnace contain a number of openings used in working the process for spreading the ore charge, drawing off the slag, etc., and one or more tap holes are provided for tapping the matte (Fig. 3).

The furnace walls and roof are constructed of highly refractory bricks with an outside casing of ordinary bricks, and the whole is bound together with steel girders placed vertically and tied together by rods. The charging of this furnace takes place from hoppers situated above openings in the roof near the side walls and extending half the length of the furnace from the firing end, and hot, partially roasted concentrate is often used. The charge melts down and reactions take place between oxide of copper and sulphide of iron present whereby the whole of the copper is converted into sulphide, according to the equation :

$$Cu_2O + FeS = Cu_2S + FeO.$$

The oxide of iron thus formed, together with that already in the roasted charge, combines with the silica in the roasted concentrates, and in the converter slags added to the charge for copper recovery, together with silica added to the charge to provide the correct amount necessary for slag formation. The copper matte containing all the copper present as sulphide together with any excess ferrous sulphide forms a layer on the bottom of the furnace, and the slag, being of lower specific gravity, floats on the top. The slag is skimmed from the top of the charge and the matte removed from the tap hole as required.

Furnaces 147 ft. long by 23 ft. wide have been used in Anaconda, and with five coal-dust burners per furnace, 760 tons of charge have been smelted in 24 hours with a consumption of 100 tons of coal dust.

In pulverised coal or oil firing, the fuel is burnt to give as short a flame as possible and the result is a high temperature peak in the furnace. The resulting increased tonnage smelted confirms the view that heat transfer in a reverberatory furnace is mainly by radiation. The shape of the furnace has undergone a gradual change to allow the rapid evacuation of the combustion gases without unnecessary draught, the furnace being run on something approaching a balanced draught. The reactions taking place in reverberatory furnaces, especially those between iron sulphide, sulphur dioxide, and copper oxides, have been studied by A. C. Halferdahl (Ind. Eng. Chem. 1930, **22**, 956).

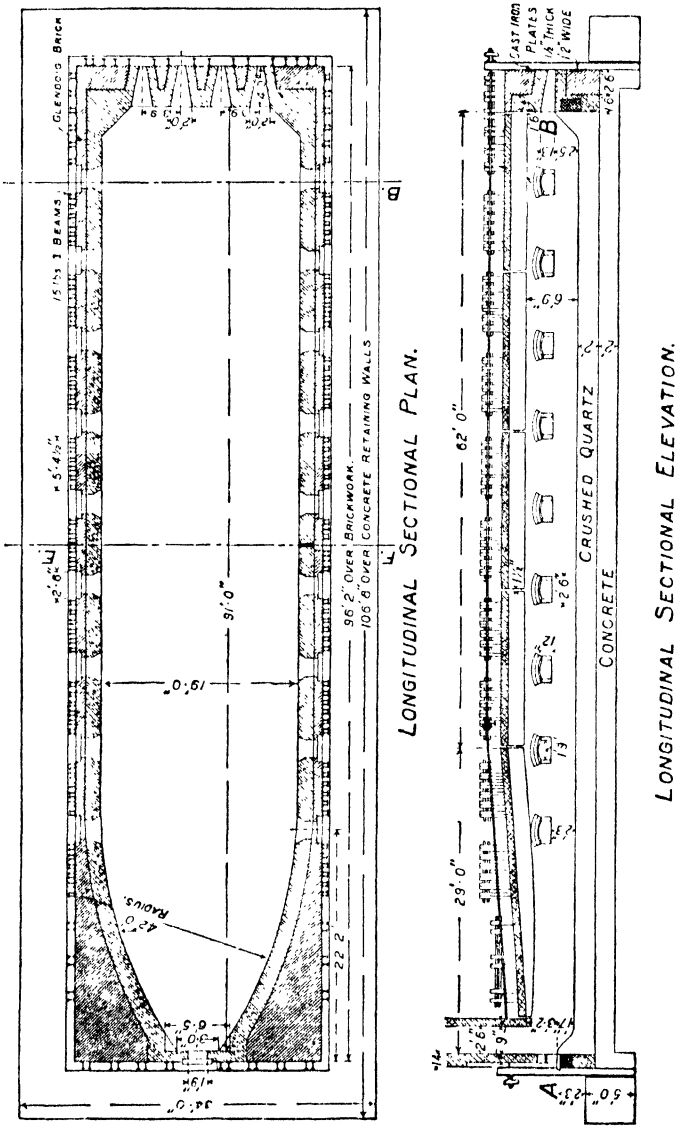

LONGITUDINAL SECTIONAL PLAN.
LONGITUDINAL SECTIONAL ELEVATION.
CRUSHED QUARTZ
CONCRETE
CAST IRON PLATES 1/2" THICK 12" WIDE
15" I BEAMS
96'2" OVER BRICKWORK
106'8" OVER CONCRETE RETAINING WALLS
91'0"
19'0"
34'0"
62'0"
29'0"
22'2"
5'4 1/2"
2'6"
B
E
A

FIG. 3.

The object to be attained in this operation in the reverberatory furnace is the same as in the blast furnace, viz. the production of a matte suitable for recovery of copper and a slag of easy fusibility and as low in copper as possible.

2. TREATMENT OF THE MATTE FOR THE PRODUCTION OF CRUDE COPPER.—It has already been pointed out that the matte consists of cuprous sulphide Cu_2S, with varying proportions of ferrous sulphide, FeS, and the further treat-

ment of this matte involves the elimination of the sulphur and iron, leaving the copper in the metallic state. This operation was formerly carried out in two stages in two or more separate furnaces ; the first stage consisted in removing the FeS and obtaining fairly pure Cu_2S or *white metal* and involved the partial roasting of the matte leaving only sufficient sulphur to combine with the copper, and the remelting of the whole with silica to form a slag with the whole of the iron present. The second stage consisted in partially roasting the white metal until a certain amount of copper oxide was formed and remelting the whole together, causing the following reactions to take place :

$$Cu_2S+2Cu_2O=6Cu+SO_2$$
$$Cu_2S+2CuO=4Cu+SO_2$$

The first reaction is the most important as representing the change which takes place in the largest proportion of the material. These processes were mainly carried out in reverberatory furnaces.

The reactions indicated above are now practically always brought about by the " converter " or " Bessemer " process.

The converter consists of a vessel formed of steel plate with a lining of basic material, magnesite bricks, or burnt magnesite. Formerly, a silicious lining was used which took part in the reactions by supplying the silica for the formation of the slag with the ferrous oxide formed. This method necessitated the frequent relining of the converters, which became expensive, so that basic-lined converters are now practically always used, the necessary silica being supplied for each charge. The form of the vessel is more or less cylindrical with the axis of the cylinder placed either horizontally or vertically. In the horizontal form the converter is somewhat barrel-shaped, and a horizontal airbox is attached to one side of the vessel for the supply of air to the charge. In the vertical form (Fig. 4) a shallow circular airbox is attached on the outside at the bottom of the vessel. Air at a suitable pressure is supplied to the airboxes as required and the supply is controlled by suitable valves. The vessel is supported on trunnions or friction rollers and is capable of being rotated by electric or hydraulic power. The vessel is provided with a suitable aperture serving the purpose of a charging opening through which the matte to be treated is poured in a molten condition, also of an outlet through which the products of the operation are poured, as well as being an escape for the gases produced in the process. Charging of the converter with matte is effected by means of a launder direct from the furnace or settler or by tapping these first into a ladle handled by an overhead crane which conveys it to the converter.

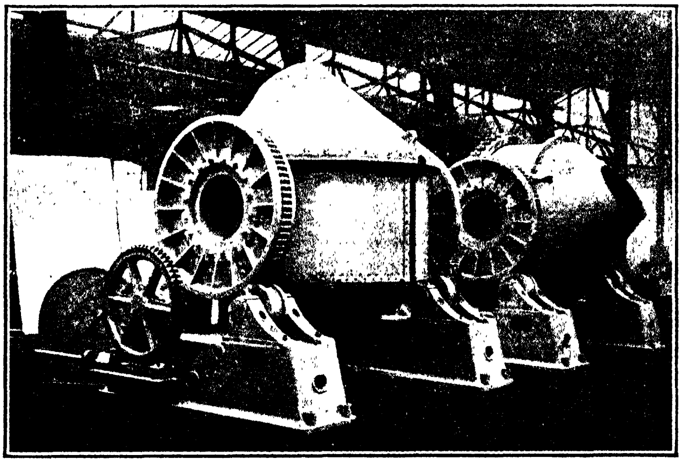


FIG. 4.

In the case of a basic-lined converter, after drying and heating up the lining, a charge of molten matte is poured in together with the necessary silica to flux the oxide of iron, the converter having been tilted into a suitable position for receiving it. The blast is then turned on and the converter tilted over so that the tuyères are brought beneath the surface of the matte and the air, being forced through the molten sulphides, causes a rapid oxidation of both constituents of the ferrous sulphide. The sulphur is oxidised to sulphur dioxide and the iron to ferrous oxide, which is immediately converted into slag by combination with the silica present, forming ferrous silicate. As the oxidation proceeds, the temperature of the charge increases and the operation is continued until practically the whole of the iron sulphide has been oxidised and the contents of the converter consist of cuprous sulphide and slag. The converter is now turned over and the slag run off into ladles and returned for re-treatment in matte furnaces for the recovery of the copper it contains. After pouring off the slag, the converter is again turned into the blowing position when the second stage of the oxidation is commenced. The passage of the air through the molten cuprous sulphide brings about the oxidation of a portion of that material to cuprous oxide which immediately reacts with unaltered cuprous sulphide producing an equivalent quantity of metallic copper in accordance with the reactions already given. This action continues until all the cuprous sulphide has been decomposed and the contents of the converter consist of metallic copper, any small quantity of slag on the surface of the copper is skimmed off for retreatment. The metallic copper is then poured by tilting the converter. As soon as the copper has been poured, the converter is ready to receive another charge and the operations are repeated.

Very large basic-lined converters are now being used, and the first stage is often carried out by several separate additions of matte. For example, 30 to 40 tons of matte may be poured into the converter followed by 3 tons of silicious ore which may itself be cupriferous. The blast is then turned on; for the first few minutes a pressure of only 5 lb. is used, and after the matte and silica have thoroughly intermingled, the blast pressure is increased to about 12 lb. per sq. in. When the silica has been fluxed by the iron oxide the converter is turned down and the slag poured off. A further charge of 10 tons of matte and sufficient silicious ore is now added and the blow resumed. This removal of slag and additions of matte and silica are continued until sufficient white metal or cuprous sulphide has accumulated in the converter to be blown to metal in the usual way.

For normal converter practice matte containing 40–45% copper is desired, but the conversion of low-grade matte containing 22% **Cu**, 45% **Fe**, 24% **S** is described by H. R. Potts (Trans. Inst. Min. Met. 1928–29, **38**, 431). The charge per blow consists of 21 tons matte, 4 tons flux, and 3 tons copper precipitate from another process. The charge is blown in a magnesite-lined converter, a temperature of 1,400° being maintained. The blister copper obtained weighs about 5 tons per blow and about 22 tons of slag high in magnetic oxide, and containing 3·4% Cu_2S and 0·5% Cu_2O are formed.

3. Refining.—The method of treatment to be adopted in this operation depends upon whether (*a*) the copper is practically free from gold and silver and from excessive amounts of deleterious elements, or (*b*) the copper contains appreciable quantities of gold and silver or contains undue quantities of deleterious elements.

If the metallic copper produced by the operations described under (1) and (2) comes under the description (*a*) above, it can be refined by furnace treatment only; if it comes under (*b*) it must be refined electrolytically in order to recover the gold and silver or to obtain it free from the impurities, and the electrodes of purified copper are then treated in a refining furnace.

Under (*a*) the furnace employed is of the reverberatory type, and the removal of the impurities is effected by slowly melting the pigs of copper under highly oxidising conditions and maintaining this condition until the impurities are oxidised and removed, either by volatilisation or by passing as oxides into the copper silicate slag formed. The oxidation of the impurities is facilitated by the fact that metallic copper has the property of dissolving a small proportion of cuprous oxide, which compound is brought into contact with the elements to be oxidised under very favourable conditions of fluidity.

The oxidising condition of the bath of molten copper is maintained until the impurities are removed as far as practicable, and the copper contains a maximum quantity of dissolved cuprous oxide. In this condition a cast ingot shows a depression on the surface and the product is known as " under-poled " or " dry " copper. After removal of the slag the next stage consists in reducing the greater portion of the dissolved cuprous oxide by covering the surface with carbon and depressing poles of green wood below the surface of the metal, when considerable agitation takes place, and the cuprous oxide is subjected to the reducing action of the gases given off by the pole. This process is continued until only a small quantity of cuprous oxide remains and the copper attains the physical condition known as " tough pitch," when it is ladled out into moulds of any required shape or run out into a large ladle and thence into moulds. In this condition the ingots have a fairly flat surface. If the poling be carried on too long, so that the whole of the oxide present is reduced, the ingots show a rising along the centre of the top and the metal is known as " over-poled."

The largest refinery plant in this country is at Prescot, where copper is refined for British Insulated Cables, Ltd., from blister copper imported from Roan Antelope Copper Mines, Ltd. The reverberatory furnaces used are 33 ft. long, 13 ft. wide (hearth size) and of 190 tons capacity, pulverised coal being used as fuel. Waste heat boilers are placed at the exhaust end and reduce the temperature of the waste gases to 200°. Fuel consumption for refining and steam raising amounts to 14% of the metal cast, as compared with 50% for refining only, in the smaller furnaces (Mining J. 1938, **201**, 452).

Under (*b*) the copper is refined electrolytically. This process depends for its operation upon the fact that if an electric current is caused to pass through a solution of copper sulphate, the copper in the solution is deposited at the cathode while acid is set free at the anode. If the anode is composed of metallic copper, then the acid set free at its surface immediately dissolves an equivalent portion of copper which passes into solution and is, in turn, deposited at the cathode, and the process thus becomes continuous so long as the current passes and there is copper at the anode to be dissolved. Assuming that the copper sulphate solution is properly made up and maintained, and the voltage and current are suitably adjusted, then only copper will be deposited at the cathode, while the gold and silver and all the impurities contained in the copper anodes will either remain as insoluble slime collected at the bottom of the vessel in which the operation is conducted or will pass into the electrolyte.

Gold, silver, and lead pass entirely into the slime; other elements, such as iron, zinc, and nickel, pass wholly into the solution, and others are to be found partly in the slime and partly in the electrolyte. The cathode surface to start with is a very thin sheet of electro-deposited copper, and when sufficient copper has been deposited on its surface it is removed from the bath and is melted down in reverberatory or other furnaces. The copper to be refined is cast into anode plates about 36 in. square and 2 to 3 in. thick, and a number of these are hung in a lead-lined wooden tank and are suitably connected to the positive pole of the electric supply. Alternating with these anode plates are hung the cathode sheets connected with the negative pole. There are two methods of connecting up, viz. “ in series,” in which the anodes and cathodes are connected in pairs, and “ in parallel,” in which all the cathodes are connected with the positive pole of the circuit and all the anodes with the negative pole. The parallel system is now generally used. There has been a tendency towards more acid electrolytes than formerly, 180–220 g. of free sulphuric acid with 35–43 g. of copper per litre being quite common practice. The current density used varies from 1·45 to 3 amp./dm.^{2} The influences of temperature and composition of the electrolyte on the resistance and on the anodic and cathodic polarisation have been determined by E. W. Rouse and P. K. Aubel (Trans. Electrochem. Soc. 1927, **52**, 189). The results show that there is a decided drop in the cell voltage with rise in temperature and with increase in acidity. The addition of glue raises the cathodic polarisation, 10 mg. per litre raising the total cell voltage by 60%. The electrolyte is caused to circulate and after it has been used for some time, a certain proportion must be removed regularly for purification. A quantity of anode copper remains undissolved, and when the tank is to be cleaned, this is taken out for remelting and casting into new anodes; the solution is run off and the slime is removed. This latter is washed and dried, any large particles of copper are removed by sieving, and the fine slime is then treated for the recovery of any gold and silver it may contain.

Wet Methods.—With certain ores and residues and under certain conditions, wet methods of extracting copper may be more suitable than smelting methods, and extensive plant are in operation in which new methods or modifications of the old methods are used.

The wet extraction of copper consists of leaching the ore with a suitable solvent either in the natural condition or after roasting and in a suitable state of sub-division, in heaps or in vats fitted with false bottoms and precipitating the copper from the solution by various methods. Wet processes are specially suitable for the treatment of low-grade oxidised ore and for oxidised tailings, but have also been successfully applied to the treatment of material containing the copper as sulphide.

At Rio Tinto the massive cupriferous pyrites are treated as mined; large heaps of the mineral are allowed to oxidise slowly under the action of air and moisture and the copper sulphate thus formed is washed out and the copper precipitated on metallic iron.

In some cases dilute sulphuric acid leaching with subsequent precipitation of the copper on iron or by electrolysis is followed but for this to be successful the copper minerals must be readily soluble in the acid and the gangue minerals must be insoluble. When carbonates of lime and magnesia are present sulphuric acid leaching cannot be used. When sulphuric acid leaching is used followed by electrolytic deposition of the copper the regeneration of the sulphuric acid yields a solvent suitable for further leaching operations.

Dilute solutions of ammonia associated with ammonium salts have been used as leaching liquors, as oxide of copper is soluble in such solutions forming copper ammonium compounds, and solutions of cupric ammonium compounds are capable of dissolving metallic copper, yielding cuprous ammonium compounds which are oxidised to cupric compounds by air or other oxidising agents. On distillation the copper ammonium solutions yield ammonia which can be used again and copper oxide which is reduced to metallic copper in reverberatory furnaces.

The method has been used at the Bwana M‘Kubwa mine in N. Rhodesia, where the crushed ore is heated to 350° in a gas-fired rotary tube furnace, the product being passed to a closed chamber where it meets a current of producer gas which reduces the copper compounds to cuprous oxide and metallic copper. The material thus prepared is leached with cupric ammonium carbonate solution. Copper and ammonia are recovered from the liquors by boiling. Melting down of the copper precipitate thus obtained yields a marketable product containing about 99·88% Cu.

In the Neil process (Eng. and Min. J. 1908, **85**, 556) solutions of sulphur dioxide have been used for the extraction of copper from oxidised or roasted sulphide ores. The ground material is treated in revolving barrels with water, and sulphur dioxide is passed through the mixture *via* one of the trunnions. The solution thus obtained is heated with steam, when about 65% of the copper in solution is precipitated as cupro-cupric sulphite and the remaining copper is precipitated on iron.

The Longmaid and Henderson process has been largely used for the treatment of the residues from the pyrites burnt for the manufacture of sulphuric acid. The residue consists of ferric oxide and is known as burnt pyrites or *blue billy*, and may contain up to 3% copper. The process consists in mixing this material with about 12% salt and re-calcining, during which process the copper is converted into soluble cupric chloride; this compound is obtained in solution by lixiviation with water and the copper is precipitated on iron. Any silver present in the pyrites is also obtained in the brine solution and may be recovered by the Claudet process.

The original Hunt and Douglas process consisted in heating ores containing carbonates or oxides of copper and roasting ores containing sulphide of copper, as for its success it was necessary for the metal to be present as cupric oxide. The ore was then treated with a solution of sodium or calcium chloride together with ferrous sulphate, which yielded ferrous chloride solution by means of which cupric oxide was converted into cupric and cuprous chlorides, both of which are soluble in strong solutions of chlorides:

$$3CuO+2FeCl_2=2CuCl+CuCl_2+Fe_2O_3$$

The solution thus obtained was passed over metallic iron for the precipitation of the copper and regeneration of ferrous chloride. The difficulties met with in this process were connected with the tendency to the formation of basic copper salts, the difficulty of separating the solution from the residue and the impossibility of recovering any silver present.

An improved process consists in dissolving the copper oxide by leaching with sulphuric acid, adding ferrous or calcium chloride to the solution to convert the copper sulphate into chloride, and then passing sulphur dioxide to precipitate the copper as cuprous chloride:

$$CuCl_2+CuSO_4+SO_2+2H_2O=2CuCl+2H_2SO_4$$

The cuprous chloride is separated for further treatment, the sulphur dioxide in solution is eliminated by blowing in hot air, and the residual sulphuric acid is available for the treatment of further quantities of ore.

The Canadian Hydrometallurgical Laboratory has applied the ferric chloride leaching process to high-grade iron-copper sulphide concentrates which have been reduced to mono-sulphides by heating in a neutral atmosphere to 600–700°. Precipitation of the copper from the leach liquors is effected by means of electrolytic iron produced in a later stage of the process. The ferrous chloride solution thus obtained is purified by means of ferrous sulphide, then electrolysed for production of electrolytic iron and the ferric chloride re-formed is returned to the leaching tanks (Canada Dept. Mines, Ore Invest. 1927, 138).

W. G. Murray (Chem. Eng. Min. Rev. 1929, **22**, 52) has shown that ferrous sulphate solution in the presence of air dissolves copper fairly readily from malachite ores but has little action on chrysocolla or cuprite. In the absence of air no copper is dissolved from malachite, showing that the solvent action is due to the oxidation of ferrous to ferric sulphate and subsequent hydrolysis of the latter.

The factors which govern the removal of soluble copper in the leaching of copper ore have been reported upon by J. D. Sullivan and A. J. Sweet (U.S. Bur. Mines, Tech. Paper 453, 1929), who recommend that leaching should be carried out at night, as the colder solutions then penetrate more rapidly into the particles of ore. Washing, on the other hand, should be carried out in the daytime, as the higher temperatures then ruling favour diffusion outwards of the copper salts. M. Guggenheim and J. D. Sullivan (*ibid.* Tech. Paper 472, 1930) show that alternate wetting and drying effect more rapid removal of the copper than does flood washing, as the intermediate drying periods tend to bring the copper salts to the surface of the particles very quickly, thus facilitating subsequent removal by washing.

PROPERTIES.—Copper is the only red metal, its properties are appreciably influenced by the presence of other elements in the metal, and the following types of copper are those chiefly used in the industries:

High Conductivity (" *HC* ") *Copper.*—This is copper of high purity usually containing 99·9% or more of copper. It is used for electrical purposes and where high thermal conductivity is specially important.

Best Select (" *BS* ") *Copper.*—This is refined copper containing small quantities of various impurities usually sufficient to prevent it from quite conforming to the conductivity standard for HC copper. It is suitable for a wide range of applications.

Arsenical Copper.—This is copper containing up to about 0·5% arsenic. Its conductivity is lower than that of HC copper. For certain reasons dealt with later, arsenical copper is widely used for engineering and general purposes.

The above types of copper usually contain a small quantity of oxygen and are then known as tough-pitch HC, BS, or arsenical copper. For certain purposes, as for welding and pipe manufacture, copper free from oxygen is most suitable and there is available " deoxidised " or " oxygen-free " copper of the various grades. In general, the mechanical properties of the above types of copper are not greatly different (Copper Data, Copper Devel. Assoc. No. 12, 1935).

Copper possesses the properties of malleability and ductility to a very high degree, so that it can be rolled into thin sheets and drawn into fine wire. As a result of cold work the metal becomes harder and eventually brittle, but its malleability and ductility are regained by an annealing operation, and after this it is immaterial whether the metal be slowly cooled or quenched in water. For practical purposes a temperature of about 200° is considered the minimum for annealing pure commercial copper though the presence of small quantities of certain elements, such as silver, nickel or arsenic, necessitates raising the temperature considerably. Annealing at 200° is very slow in its effects, and in practice it is more general to anneal for a short time at a temperature of 500–600°. Too prolonged a heating or the use of too high a temperature is to be avoided. For pure commercial copper the tensile strength varies between 10 and 11 tons per sq. in. as cast, between 20 and 26 tons after cold working, and between 14 and 15 tons on annealing after work. The elongation varies between 25 and 30% on 2 in. in the cast state, between 5 and 20% after cold working, and between 50 and 60% on annealing. The Brinell hardness number likewise varies between 40 and 45 in the cast state, between 80 and 100 after cold-working, and between 45 and 55 after annealing. Its sp.gr. after working and annealing is 8·93, but that of commercial copper usually ranges from 8·2 to 8·8, the lower figures being due to porosity. Its m.p. is 1083°, and when melted in the air it is rapidly oxidised with the formation of cuprous oxide which dissolves in the metal reducing its freezing-point to 1,065°, at which temperature the copper-cuprous oxide eutectic solidifies containing 3·5% cuprous oxide. The metal boils at 2,325°. Copper crystallises in the cubic system; well-formed octahedral crystals are found in nature and are sometimes formed during electrolysis. The electrical conductivity of copper is very high and is taken as a relative standard of 100; it compares very favourably with other metals in this respect, being second only to silver with a relative conductivity of 106 and is followed in the scale by gold with a relative conductivity of 72. The electrical resistivity of copper is 1·7241 microhms per $cm.^3$ at 20°. These resistance and conductivity values apply only to copper after it has been worked and annealed; bars as cast may have a conductivity of 95 and upwards, but complex castings may be as low as 80. The electrical resistance of copper, as of all metals, varies with the temperature and this variation is sufficient to cause the conductivity of HC copper to fall to about 75% of its value at 20°, when the temperature is raised to 100°. The conductivity of copper as of all pure metals is largely affected by the addition of other elements; phosphorus, silicon, iron, arsenic or beryllium when present in quantities less than 1% reduce its conductivity from 100 to 30. The presence of small quantities of silver and cadmium has little effect and that of oxygen in the amounts present in commercial coppers is negligible. The thermal conductivity of copper is also high, this metal as 100 being only second to silver at 108, and is followed by gold at 76. The thermal conductivity of HC copper is 0·92 g. cals. per cm./cm./second/degree C. at 20°. The specific heat at normal temperatures is 0·092 cals. per g. per degree, but with increase of temperature it rises, the value at 200° being 0·098 cals. The coefficient of thermal expansion is $16{\cdot}6\times10^{-6}$ per degree. Dry air has no action on copper at normal temperatures, but under ordinary atmospheric conditions the metal becomes slowly tarnished with an oxidised film which changes in time to a mixture containing sulphate and carbonate (*v.* Co-ordination compounds, this vol., p. 336). This mixed salt deposit is normally green and forms the well-known patina of copper, and it serves as a protection to the underlying copper. When heated in air a superficial film of oxide is formed which remains adherent and serves as a protection against further attack up to a red heat, but at higher temperatures serious scaling results. Sulphur dioxide when dry either in the gaseous or liquid condition has no effect on copper. When the sulphur dioxide is in a moist, dilute state in contact with the metal it forms a protective covering of basic sulphate. Carbon dioxide has no action on copper in the dry state. In the presence of moisture the action is very slow and the resulting product, as in the case of atmospheric action, forms a protective skin. Copper is rapidly attacked by chlorine, and ammonia also readily attacks the metal. Ordinary water supplies have no action on copper, as an oxidised superficial tarnish soon develops which acts as a protection to the underlying metal. Waters which are acid in reaction may prevent the formation of this protective film and slight dissolution of the copper may result. Nitric acid attacks copper violently, very dilute hydrochloric acid has little effect, but the concentrated and moderately dilute acid attack the metal, the action being more rapid if the acid be hot. The presence of air is also an important factor in promoting the action. Cold sulphuric acid has little action on copper, but the hot concentrated acid rapidly attacks the metal. Acetic acid has little action on copper, especially in the absence of oxygen, and the metal is used largely for stills, rectifiers, piping, receivers etc., for this acid. Lactic, tannic, formic, and other organic acids have little or no action on the metal. Copper is resistant to dilute solutions of the alkalis, soda, and potash, but not to the action of concentrated solutions. It is fairly resistant to the action of sea-water and of solutions of many salts, but should not be used in contact with inorganic salts which are oxidising agents, such as dichromates, persulphates, perchlorates or ferric chloride. Hydrocarbons, such as petroleum, benzene, etc., have no action, neither have the alcohols, esters, and many other organic materials.

The effects of various impurities on the properties of pure copper have been investigated for the British Non-Ferrous Metals Research Association at the National Physical Laboratory, and the following is a summary of the results:

Oxygen has a relatively small effect on the properties of pure copper, and is neither seriously deleterious nor remarkably beneficial. The mechanical properties are not much affected by small quantities and a metal containing 0·1% differs very slightly from pure copper. The electrical conductivity does not fall rapidly with additions of oxygen, and values exceeding 100% of the International Standard are obtained in annealed specimens containing less than 0·1%. The relatively small effect of oxygen is due to the fact that the solubility of cuprous oxide in copper is extremely low and may be considered as nil (Hanson, Marryat and Ford, J. Inst. Metals, 1923, **30**, 197).

Arsenic.—In the absence of other impurities, copper containing up to 1% arsenic is very difficult to cast and it is difficult to obtain sound castings. A slight amount of unsoundness does not appear to have any harmful effect on the working properties of the metal, which is remarkably malleable and ductile, and can be worked hot or cold to almost any desired extent. It has been found possible by continuous cold-rolling to reduce cast ingots $1\frac{9}{16}$ in. in diameter containing up to 1% arsenic to thin strip only 0·004 in. thick. Even when the arsenic is over 7% the ingots were capable of withstanding a considerable amount of cold hammering without developing cracks. Mechanical tests show that arsenic has but a slight hardening effect on copper; as the arsenic content is raised from 0 to 1·04% the tensile strength of the annealed material rises only slightly, from 14 to 15 tons per sq. in. The

Brinell hardness of annealed arsenical copper is practically unaffected by the arsenic up to 1%, but the hardness of cold-worked material increases with the arsenic content. The effect of arsenic on the electrical conductivity of copper is very great, it is much greater than the effect of oxygen and very distinctly greater than that of iron. The effect is such that arsenic must be excluded as rigidly as possible from high-conductivity copper. Arsenic appears to reduce the crystal size in castings, but this effect is not appreciable in worked and annealed material. The solubility of arsenic in solid copper is about 7·25%; this solubility changes very little with temperature (Hanson and Marryat, J. Inst. Metals, 1927, **37**, 121).

Arsenic plus Oxygen.—A series of alloys containing up to 2% arsenic and 0·1% oxygen has been examined. The presence of a little oxygen greatly improves the casting properties of arsenical copper and no difficulty is experienced in obtaining sound castings with a relatively high density. Oxygen has a harmful effect on the cold-working properties of copper which is reduced by the presence of arsenic. Arsenical copper is not suitable for severe cold-working unless the arsenic concentration is at least 10 times that of the oxygen. Copper containing arsenic and oxygen can be rolled hot without difficulty. The mechanical tests of rolled and annealed bars of good quality differ little from those of copper containing the same amount of arsenic without oxygen, provided that the material has not been damaged by over-rolling; the tensile strength rises slightly and the elongation falls slightly with increase of arsenic content. The electrical conductivity is practically identical with that of copper containing the same amount of arsenic without oxygen (Hanson and Marryat, *ibid.* 1927, **37**, 144).

Iron.—Solid copper will dissolve about 4% iron at 1,080°, but the solubility decreases as the temperature falls. Within the limits of solubility, the effect of iron is considerable, especially on the electrical resistance, which increases rapidly as the iron content is raised. When the iron content exceeds about 0·2% the effect on the resistivity depends largely on the heat-treatment of the metal. The tensile strength is raised by 2% iron from 14·5 to 20 tons per sq. in. Iron has no great embrittling effect and copper containing iron can be rolled with ease. Iron is a deoxidiser for copper, but it creates difficulties during casting owing to the formation of films which destroy the continuity of the metal (Hanson and Ford, J. Inst. Metals, 1924, **32**, 335).

Bismuth.—The solid solubility of bismuth in copper is less than 0·002%. Small quantities of bismuth adversely affect the rolling properties of copper, particularly during hot-rolling. The limiting amount for hot-rolling of bar appears to be less than 0·01% and in all cold-rolling experiments the material fractured when more than about 0·05% was present. For severe cold-work bismuth should be excluded from copper; for most other purposes 0·005% may be regarded as the maximum (Hanson and Ford, J. Inst. Metals, 1927, **37**, 169).

Antimony.—Annealed copper will hold as much as 10% antimony in solid solution. Samples containing up to 0·47% can be hot-rolled satisfactorily, but those containing 0·85% are hot-short and samples up to this figure can be cold-rolled. The presence of quite small amounts of antimony, *e.g.* up to 0·22%, has a remarkable effect on the tensile properties, an annealed rod containing this amount giving 14·9 tons per sq. in. with 67% extension, while a hot/cold-rolled specimen will give 24 tons per sq. in. with 19% extension. Antimony has no pronounced effect on the toughness of copper and the fatigue properties are improved by the addition of antimony up to 0·47% hot-rolled. With this composition a safe range of stress of ± 7·8 tons/in.^{2} was obtained as compared with ±5 to 6 tons/in.^{2} typical of high-quality copper. Antimony lowers the electrical conductivity of copper very considerably but is approximately only half as deleterious in this respect as arsenic (Archbutt and Prytherch, J. Inst. Metals, 1931, **45**, 265).

Antimony plus Arsenic.—Within the limits studied 0·05–0·5% each of antimony and arsenic, and under 0·02% oxygen, copper can be hot-rolled without difficulty, so that arsenic assists the hot-rolling of copper containing antimony. The addition of antimony to arsenical copper improves its tensile strength both at ordinary temperatures and at 250°. In annealed rod containing 0·49% antimony and 0·059% arsenic, 15·6 tons per sq. in. was obtained at room temperature and 13 tons at 250°. With cold-rolled strip containing 0·5% antimony and 0·53% arsenic a tensile strength of 37·2 tons/in.^{2} with 2·3% extension was obtained. The fatigue properties of copper containing 0·5% antimony and 0·5% arsenic are similar to those given above for antimonial copper (*idem.*, *ibid.* 282).

Phosphorus.—In small quantities phosphorus produces soundness in, and removes oxides from copper. With 0·04% and more of phosphorus, the densities of cast copper approach those of rolled bars. The hardness of cast ingots increases with increasing phosphorus content. The limiting phosphorus content for hot working lies between 0·95 and 1·2%, whilst the limiting content for cold-rolling is 0·79–0·95%. Phosphorus raises the tenacity of rolled copper both at ordinary temperature and at 250° without marked decrease in ductility. Small amounts of phosphorus have a pronounced effect in raising the fatigue range of copper, and its toughness remains unimpaired. The softening temperature of cold-rolled copper is raised by phosphorus which has a seriously detrimental effect on electrical conductivity. The solubility of phosphorus in solid copper increases with rise of temperature from 0·5% at 282° to 1·0% at 682°. A slight age-hardening effect occurs in copper containing phosphorus when quenched from 690° and tempered at 400–450°, the maximum effect occurring with 0·95% phosphorus; the Brinell hardness of a quenched rolled strip of this metal increases from 43 to 52, but no corresponding effect on tensile strength is obtained (Hanson, Archbutt, and Ford, J. Inst. Metals, 1930, **43**, 41).

Detection and Estimation of copper, *see* Chemical Analysis, Vol. II, 566*b*, 580*c*, 586*a*, 656*c*, 671*b*.

Uses of Copper and its Alloys.—Copper and its alloys have very wide applications in engineering and industries generally, these applications being advantageous owing to the various special properties of the metal. In the first place they are possible owing to the ease of working of the metal; it can be fabricated by cold-working, such as rolling, drawing, pressing, etc., by hot-working, such as pressing, extrusion, forging and stamping, and by machining; it can be joined by welding, brazing, or soldering.

Its high electrical conductivity renders it suitable for cables for transmitting electricity, for windings of electrical machines and apparatus, for electrodes and connections for welding machines and furnaces and for lightning conductors and earthing systems. Its high thermal conductivity makes it suitable for radiators for cooling various liquids, for refrigerator tubes, coils and vessels, for radiators for heating purposes, etc., for locomotive fire boxes, chemical plant, stills, evaporators, etc. Its resistance to rusting and corrosion makes it suitable for various types of chemical plant, brewing plant, roofing, and tubing for water distribution, and some of its alloys for parts of marine machinery, propellers, pumps, etc.

Various alloys in which copper is the chief constituent are largely employed for applications requiring increased strength and other special properties. The most important of these alloys are the brasses or alloys of copper and zinc; other important groups are the bronzes, or alloys of copper and tin, the aluminium bronzes or alloys of copper and aluminium (*see* Aluminium), and the copper-nickel alloys.

Copper is also alloyed with certain metals to act as a hardener as in the case of standard silver and standard gold.

Certain elements are added to metallic copper in order to improve its properties, and of these an important class is known as deoxidisers. Tough pitch copper generally contains from 0·025 to 0·08% oxygen, and for making intricate castings, for welding, and for certain other purposes copper as low as possible in oxygen is desirable. The deoxidisers commonly used are phosphorus, silicon, lithium, magnesium, beryllium and calcium; these are added to the molten metal, when they combine with the oxygen and eliminate it, usually by slagging off. To remove all the oxygen it is generally necessary to add a small excess of reagent which remains in the copper and may have an adverse effect on the electrical and thermal conductivity.

Beryllium is not only used as a deoxidiser, but also as a definite alloying element, forming heat-treatable alloys of engineering importance. Copper containing 2·25% Be is known as *beryllium bronze*; for its heat treatment it is first annealed by soaking at 800°, followed by quenching in water; it is then hardened by a subsequent precipitation treatment by heating for a controlled period at 250–300°. When heat-treated after cold working, tensile strengths of over 80 tons per sq. in. have been reported. A considerable merit of this material is its high fatigue limit under corrosive conditions.

Copper containing cadmium (approximately 1%) is of importance on account of its combining high strength with conductivity.

Arsenical copper containing 0·3 to 0·5% arsenic is of great importance and most copper products made in Great Britain other than electrical equipment are made from this material. Additions of up to 0·5% arsenic improve the tensile strength of annealed copper by somewhat less than 1 ton per sq. in., and only slightly increase its hardness value. In the cold-worked condition, however, the tensile strength is increased by 2 tons per sq. in. and the Brinell number is 15 higher. The chief effect of this addition of arsenic is to raise by 100° the temperature at which softening upon annealing first occurs and to slightly increase the strength at elevated temperatures; these two features have been responsible for the adoption of arsenical copper for a large number of applications such as locomotive fire-boxes, etc.

Compounds of Copper.

Oxides.—Six oxides of copper have been reported of which only two are of importance, namely cuprous oxide, Cu_2O, and cupric oxide, CuO. Cuprous quadrantoxide, Cu_4O, has been considered as being formed by the addition of a solution of copper sulphate to a cooled dilute solution of stannous chloride in caustic potash. It is an olive-green powder which rapidly absorbs oxygen from the air. According to Moser, however, this product is really a mixture of cuprous oxide and metallic copper (Z. anorg. Chem. 1909, **64**, 200). Copper trientoxide, Cu_3O, is stated to have been obtained as a hard, yellowish mass by heating cupric oxide to over 1,500° (Bailey and Hopkins, J.C.S. 1890, **57**, 269). It is probably a solid solution of copper in cuprous oxide. Copper sesquioxide, Cu_2O_3, has been reported to have been formed by passing chlorine into a strong solution of sodium hydroxide saturated with copper hydroxide (E. Müller, Z. anorg. Chem. 1907, **54**, 417). This oxide is not known in the free state. Copper peroxide or dioxide, CuO_2, is not known in the anhydrous form, but in the hydrated form, CuO_2,H_2O, is obtained by allowing finely-divided cupric hydroxide to stand in concentrated hydrogen peroxide at 6° for several days, the mixture being frequently shaken. A yellowish-brown precipitate is formed which, after washing with water, alcohol, and ether, is dried *in vacuo* (G. Krüss, Ber. 1884, **17**, 2593).

Cuprous oxide, copper suboxide or hemioxide, red oxide of copper, Cu_2O, occurs native as cuprite or red copper ore.

It may be prepared (1) by heating finely divided copper in air below a red heat; (2) by gently heating a mixture of 5 parts cuprous chloride and 3 parts sodium carbonate in a covered crucible and separating the oxide by lixiviation; (3) by reduction of an alkaline solution of a copper salt by sugar or certain other organic bodies, as in Barreswil's (Fehling's) solution, (4) by heating in a covered crucible a mixture of 5 parts cupric oxide and 4 parts copper filings; (5) by the electrolysis of copper sulphate solutions under certain conditions; (6) by heating cupric oxide in sulphur dioxide and treating the product with water for removal of sulphate: $3CuO+SO_2=Cu_2O+CuSO_4$ (Hammick, J.C.S. 1917, **111**, 384); (7) free from copper and cupric oxide by the electrolysis of a slightly alkaline solution of sodium chloride with copper electrodes (E. Abel and O. Redlich, Z. Elektrochem. 1928, **34**, 323).

Cuprous oxide is decomposed by most acids into a cupric salt and metallic copper; hydrochloric acid, however, converts it into cuprous chloride. It fuses at 1,235° and dissolves in molten copper rendering it brittle or " dry " when present above a certain amount, but is a most important constituent in many brands of copper. It is used in the manufacture of *ruby glass* and for the production of a red glaze on pottery, and, together with the black oxide, forms one of the *copper paints* used for painting ships' bottoms.

Cuprous oxide has been found to adsorb about 30% by weight of NO_2, which may be removed at 65–70° by an inert solvent, such as CCl_4 (Partington, J.C.S. 1924, **125**, 72, 663). The oxide has remarkable rectifying and photoelectric properties which are extensively applied in new types of photoelectric cells (*cf.* Duhme and Schottky, Naturwiss. 1930, **18**, 735).

Cuprous hydroxide, hydrated cuprous oxide, Cu_2O,xH_2O.—A yellow form of cuprous oxide is obtained by the action of alkali on cuprous chloride or by the reduction of a cupric salt by means of hydroxylamine in presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure copper. It may also be formed by the reduction of Barreswil's (Fehling's) solution in the presence of a deficit of tartrate. The yellow precipitate thus formed is not a definite hydrate but is a colloidal form of the oxide with an indefinite amount of water (Gröger, Z. anorg. Chem. 1901, **28**, 154; 1902, **31**, 326). It quickly changes to an orange or brick-red colour and can then be dried unchanged. At 300° it retains only 3%, and at a red heat it loses this water and changes into the red crystalline oxide. The yellow oxide is a powerful reducing agent, especially in ammoniacal solution. This solution, which is colourless, immediately becomes blue on exposure to the atmosphere and thus forms a delicate test for oxygen.

Cupric oxide, copper monoxide, black oxide of copper, CuO, occurs as tenorite or melaconite, especially at Lake Superior.

Cupric oxide may be prepared by heating the nitrate or carbonate to dull redness or the sulphate to a high temperature. It may also be obtained by heating finely divided copper or cuprous oxide in air or oxygen, pure oxygen acts more slowly than air owing to the protective nature of the film of oxide first formed. The oxide used for organic analyses, (but not for N estimation) may be prepared by moistening copper scale, the mixture of cuprous and cupric oxides, with nitric acid and igniting. A mixture of copper filings with twice its weight of nitric acid may be exposed to the atmosphere until all the copper is converted into basic nitrate and this ignited. E. Müller prepared cupric oxide by the electrolysis of sodium hydroxide for a long time with a copper cathode either at 12° with stirring or at 60° without stirring (Z. Elektrochem. 1903, **9**, 313).

Cupric oxide is a black powder which agglomerates when heated and fuses at 1,064° forming cuprous oxide. It is slightly hygroscopic, especially when in powder form. When heated with organic substances or certain gases it is reduced to metal. The metal produced by reduction in hydrogen always contains that gas, but if the oxide be reduced in formic acid vapour, the metal is free from hydrogen and is suitable for organic analysis (Weyl, Ber. 1882, **15**, 1138). It dissolves in acids with the formation of cupric salts. It is soluble to some extent in oils, etc., and it is for this reason that copper cooking vessels require constant cleaning.

Cupric oxide is used in ultimate organic analysis, to make green and blue glass and glazes and to some extent as a pigment. It has also been used as one electrode of a galvanic cell (Lalande and Chaperon, Compt. rend. 1883, **97**, 164).

A colloidal form of the oxide has been obtained by Paal and Leuze (Ber. 1906, **39**, 1545), which gives blue-violet solutions, and when dry retains its solubility indefinitely.

Cupric hydroxide, CuO,H_2O, may be prepared by precipitating a solution of a cupric salt by the addition of alkali and washing rapidly. The hydroxide, which is blue, is liable to turn black during washing owing to the formation of cupric oxide, and when heated with water always turns black. It may be obtained by passing an electric current through a well-stirred solution of potassium nitrate, using a copper plate as anode and one of platinum as cathode (Lorenz, Z. anorg. Chem. 1896, **12**, 436).

The hydroxide has been used as a blue pigment by paper stainers but becomes green on exposure to the atmosphere. It corresponds closely with certain highly basic carbonates sold as *verditers.*

An aqueous solution of sodium hydroxide of sp.gr. 1·345–1·370 or of potassium hydroxide of sp.gr. 1·453–1·498, will dissolve 0·78 g. of cupric hydroxide in 100 c.c., giving a bright blue solution which yields no precipitate when boiled. If a more dilute alkali solution be used the product is not stable when further diluted and subsequently boiled (E. Justin-Mueller, Compt. rend. 1918, **167**, 779).

Cuprammonium solutions are obtained by digesting freshly precipitated cupric hydroxide in ammonia solution, and H. M. Dawson and J. McCrae (J.C.S. 1900, **77**, 1257) believe that a compound $CuO,2NH_3$ or $Cu(OH)_2,2NH_3$ is formed which ionises forming $Cu2NH_3^{\cdot\cdot}$ and OH' ions, thus:

$$Cu(OH)_2+2NH_3 \rightleftharpoons Cu2NH_3^{\cdot\cdot}+2OH'$$

W. Bonsdorff has also examined the electrical conductivity of solutions of cupric hydroxide in ammonia solution and has confirmed the formation of $Cu(OH)_2,2NH_3$ when only a small excess of ammonia is present, but of $Cu(OH)_2,4NH_3$ with a large excess of ammonia (Z. anorg. Chem. 1904, **41**, 184). A blue solution is obtained by exposing the colourless solution of cuprous hydroxide in ammonia to the atmosphere, and cuprammonium solutions are prepared on a large scale by the joint action of oxygen and ammonia on copper filings at a temperature near 0°.

A saturated solution of freshly precipitated and washed cupric hydroxide in concentrated ammonia is known as "Schweizer's reagent" or *cuprammonium*, it has the property of dissolving cellulose (cotton wool, linen, filter paper, etc.), with the formation of a viscid liquid which has been used for the preparation of "Willesden papers" and for the production of "artificial silk" on a large scale. A. Froment patented the use of strong ammonia saturated with nitrogen which is claimed to dissolve cupric oxide more readily than when free nitrogen is absent (G.P. 139714, 1900), and A. Lecoeur recommends the removal of the nitrites and other crystallisable compounds from the solution by dialysis (F.P. 362986, 1906). The addition of 1–2% of polyhydric alcohols, carbohydrates, gum, etc., to cuprammonium solutions increases their stability and prevents the deposition of cupric hydroxide (Friedrich, B.P. 4104, 1909), and the presence of such substances facilitates the manufacture of the solution. Chattaway has shown (Proc. Roy. Soc. 1908, **80**A, 88) that by the reduction of a cuprammonium solution with phenyl hydrazine, copper mirrors can be deposited on glass.

Sulphides.—*Cuprous sulphide*, Cu_2S, occurs as *chalcocite* or *copper glance*. It may be prepared by heating copper to redness in sulphur vapour or by heating a mixture of copper and sulphur. It is also formed as a result of the reaction between metallic copper and certain sulphides, *e.g.* aluminium, magnesium, cadmium, etc., and E. Schütz has found that copper forms sulphide with 85% of the sulphur in ferrous sulphide when the two are heated together to 1,195° (Metallurgie, 1907, **4**, 663). It melts at 1,130° and the sp.gr. of the artificial product is 5·80. It is dimorphous and has a transition temperature at 91°.

Cupric Sulphide, CuS, occurs as *covellite* or *indigo-copper*, sp.gr. 4·60. It may be prepared by heating cuprous sulphide with sulphur at a temperature below the boiling-point of sulphur; by digesting cuprous sulphide with cold strong nitric acid or by precipitating a copper solution with hydrogen sulphide. On the large scale it is obtained as a paste by precipitating a solution of the sulphate with sodium sulphide, and this paste has been used in calico printing for the development of aniline black.

Several polysulphides of copper have been reported.

Cuprous Phosphide, Cu_3P, is formed by the interaction of copper and phosphorus, and is present in the alloy known as *phosphor-copper*, which contains from 9–15% phosphorus. Alloys containing more than this amount of phosphorus have to be prepared in closed vessels owing to the volatility of the phosphorus. They are largely used for the deoxidation of metallic copper and in the manufacture of *phosphor-bronze*. The compound Cu_3P melts at 1,022°, and forms a eutectic with metallic copper which contains 8·2% phosphorus and melts at 707°.

Cupric Phosphide, Cu_3P_2, is formed when phosphine is passed over cupric chloride or when phosphorus is boiled with a cupric salt. When heated in hydrogen it forms cuprous phosphide.

Copper Arsenides.—Copper and arsenic combine together to form several arsenides, some of which are found to occur as minerals. When copper and arsenic are heated together cupric arsenide, Cu_3As, is formed which freezes at 830°. At 710° there is evidence of the formation of an unstable compound, Cu_5As_2, with 32·1% arsenic (K. Friedrich, Metallurgie, 1908, **5**, 529).

Copper Silicide, known as *cuprosilicon*, Cu_4Si, is obtained when copper and silicon are heated together in an electric furnace (Vigouroux Compt. rend. 1896, **122**, 318; Lebeau, *ibid.* 1906, **142**, 154). It can be prepared pure by heating together 17 parts silicon and 9 parts copper in hydrogen and removing the excess silicon by means of sodium carbonate solution. It is silver white with a metallic lustre and is hard and brittle. Its sp.gr. is 7·58 and it is attacked by chlorine and *aqua regia*. It is used for deoxidising and hardening copper and certain of its alloys (*v.* Philips, Metallurgie, 1907, **4**, 587).

Copper Silicates are formed when oxides of copper and silica are fused together. Silicates are found in the various slags obtained during the smelting of copper ores, and especially in those produced in the converters and during the fire-refining of copper. The copper in these slags is readily reduced to metal by carbon in the presence of iron oxide with the formation of the corresponding iron silicate, it is also reduced by heating with metallic iron and is converted into cuprous sulphide when heated with iron sulphide. As hydrated silicates copper occurs in two minerals, viz. *dioptase* or *emerald copper*, $CuSiO_3,H_2O$, and *chrysocolla*, $CuSiO_3,2H_2O$.

Copper Carbonates.—The normal carbonate has not been prepared, but double salts of the normal cuprous and cupric carbonates with ammonium and other carbonates have been described.

Some twelve basic carbonates, varying in the ratios of $CuO : CO_2 : H_2O$ have been reported, several of which occur as minerals, the best known of which are *malachite*, $CuCO_3,Cu(OH)_2$, and *azurite*, $2CuCO_3,Cu(OH)_2$; when ground, these minerals form valuable green and blue pigments. The products obtained by the addition of sodium carbonate or other soluble carbonates to solutions of copper sulphate or nitrate are invariably basic, the degree of basicity depending on the conditions of precipitation. These basic carbonates are known as *Soda Bordeaux* and are largely used as a fungicide. S. U. Pickering (J.C.S. 1909, **95**, 1410) states that the ordinary carbonate of commerce approximates to $2CuO,CO_2,H_2O$, the formula for malachite, which contains 71·94% CuO, but H. B. Dunnicliff and S. Lal (J.C.S. 1918, **113**, 718) found on examination of thirteen samples of commercial carbonate that the amount of CuO varied from 66·16 to 78·60%, and considered that the product generally approximated to the formula of azurite; and by treatment of a solution of copper sulphate with a mixture of sodium carbonate and sodium bicarbonate they obtained a product of fairly constant composition corresponding to

$$2CuCO_3,5Cu(OH)_2.$$

Many methods have been used for the preparation of the basic carbonates of commerce, such as the conversion of scrap copper into basic chloride by the action of sodium chloride and sulphuric acid, and treatment of a mixture of this basic chloride and copper sulphate with soda solution, or by agitation of a solution of copper nitrate with chalk, the pasty precipitate obtained is washed and mixed with 8–10% of freshly burnt lime with the production of a fine blue pigment (*verditer*); the precipitate without the addition of lime is green.

Salts.—Two series of copper salts are known, *cuprous* and *cupric*. The former are mostly insoluble in water and are of little commercial importance. They act as powerful reducing agents and readily pass into the cupric condition. Cupric salts are mostly soluble and are of wide application.

Cuprous Salts.—*Cuprous chloride*, $CuCl$, may be prepared by boiling cupric chloride with hydrochloric acid and copper turnings. On the addition of water it is precipitated as white crystals. Cuprous chloride melts at about 420° into a yellow transparent mass. The dry crystals become yellowish on exposure to light; if moist they acquire a dirty violet tinge.

Cuprous chloride combines with ammonia to form three compounds, $2CuCl,NH_3$, $2CuCl,3NH_3$, $CuCl,3NH_3$. Cuprous bromide and iodide form compounds analogous to the last two (Lloyd, J. Phys. Chem. 1908, **12**, 398; *cf.* W. Biltz and W. Stollenwerk, Z. anorg. Chem. 1921, **119**, 97).

The hydrochloric acid solution of cuprous chloride, when exposed to air, absorbs oxygen and acquires a brown colour, subsequently depositing a pale bluish-green insoluble copper oxychloride, $CuCl_2,3Cu(OH)_2$, similar to the mineral *atacamite*. An identical substance, known as *Brunswick green*, is prepared by boiling a solution of copper sulphate with a small quantity of bleaching powder solution, or by exposing freely to air copper turnings moistened with hydrochloric acid.

The use of the oxychloride in preference to the sulphate for destroying mould on vines, etc., is recommended by Deletrez (J.S.C.I. 1909, **28**, 438), 200–250 g. per 100 litres of water are employed.

When a hydrochloric acid solution of cuprous chloride and potassium chloride, is treated with acetylene, a yellowish precipitate, $C_2H_2[(Cu_2Cl_2)_2,KCl]_2$, is formed. Other compounds containing cuprous oxide or potassium chloride can be obtained by varying the conditions (Chavastelon, Compt. rend. 1901, **132**, 1489). Acetylene reacts with solutions of cuprous chloride in ammonia to form a blood-red precipitate of cuprous acetylide which on dehydration has the formula Cu_2C_2 and is highly explosive (Scheiber, Ber. 1908, **41**, 3816). Its decomposition by means of acids has been used as a method of preparing pure acetylene.

Cuprous chloride in a hydrochloric acid or ammoniacal solution absorbs carbon monoxide forming an unstable compound (Jones, Amer. Chem. J. 1899, **22**, 287) which under certain conditions corresponds to $CuCl,CO,2H_2O$ (Berthelot, Ann. Chim. Phys. 1901, [vii], **23**, 32).

Cuprous Bromide, $CuBr$, is obtained by the union of its elements or by boiling a solution of cupric bromide with copper, and forms a colourless crystalline mass.

Cuprous Iodide, CuI, is the only known iodide of copper, and is found in the mineral *marshite* (Broken Hill, Australia). It is obtained as a white precipitate by adding potassium iodide to a solution of copper sulphate; in this way half the iodine is combined in the precipitate and half is liberated as free iodine; in the presence of ferrous sulphate or sulphurous acid, the whole of the iodine is precipitated as cuprous iodide. The fused salt has a sp.gr. of 5·653 at 15° (Spring, Rec. trav. chim. 1901, **20**, 79); it melts without decomposition at 628° and is practically insoluble in water.

Cuprous Fluoride, CuF, is prepared by the action of hydrogen fluoride on heated cuprous chloride; the action is complete only when the temperature is between 1,100° and 1,200°. It is also formed by the action of hydrogen fluoride on cupric fluoride, first heated to 600°, and finally raised to 1,100–1,200°. Cuprous fluoride forms a red crystalline mass which melts at 908°. It is stable in dry air, but is converted into cupric fluoride in moist air, at the same time acquiring a blue colour.

Cuprous Sulphite, Cu_2SO_3,H_2O, is obtained by passing sulphur dioxide into a hot solution of cuprous acetate in acetic acid. It forms double salts with the alkali sulphites. Cupro-cupric sulphite, $Cu_2SO_3,CuSO_3,2H_2O$, is a red microcrystalline powder.

Cuprous Sulphate, Cu_2SO_4, is obtained by the action of dry dimethyl sulphate on dry, powdered cuprous oxide (Recoura, Compt. rend. 1909, **148**, 1105). A compound of cuprous sulphate and carbon monoxide, $Cu_2SO_4,2CO,H_2O$, has been obtained by Joannis (*ibid.* 1897, **125**, 948). Péchard, by adding hydroxylamine sulphate to ammoniacal cupric carbonate, has made ammonio-cuprous sulphate $Cu_2SO_4,4NH_3$ (*ibid.* 1903, **136**, 504).

Cuprous Cyanide, $CuCN$, is obtained by adding potassium cyanide to a solution of copper sulphate, a red precipitate of cupric cyanide is first formed and on boiling cyanogen gas is given off and the white cuprous cyanide is precipitated. Cuprous cyanide forms a number of double cyanides (Grossmann and von der Forst, Z. anorg. Chem. 1903, **43**, 94).

Cuprous Thiocyanate, $CuCNS$, is obtained as a white precipitate when potassium thiocyanate is added to copper sulphate solution in the presence of a reducing agent such as sulphur dioxide, ferrous sulphate, etc. This reaction is used in quantitative analysis.

Cuprous Nitrate v. Cupric nitrate.

Cupric Salts.—*Cupric chloride*, $CuCl_2$, may be obtained as a fused liver-coloured, anhydrous mass by heating copper in excess of chlorine. In solution it may be prepared by dissolving the oxide in hydrochloric acid. It crystallises in grass-green prisms or needles containing 2 mols. of water which become pale-blue when dried *in vacuo*. The anhydrous salt is obtained on the gradual addition of concentrated sulphuric acid to a solution of the chloride (Viard, Compt. rend. 1902, **135**, 168). This anhydrous salt is very deliquescent and forms the salt containing 2 mols. of water mentioned above. It is soluble in alcohol. When cupric chloride is exposed to the air an oxychloride is formed, and when a small quantity of potash is added to an aqueous solution the oxychloride, $2CuO,CuCl_2,4H_2O$, is formed as a pale blue precipitate, this turns to a black anhydrous powder when heated, but again becomes green with absorption of 3 mols. of water when moistened. It is an intermediate product in the manufacture of *verditer* (*v.* Copper Carbonates). Some eighteen basic cupric chlorides have been reported.

Cupric Bromide, $CuBr_2$, is obtained by dissolving cupric oxide in hydrobromic acid and evaporating *in vacuo* over sulphuric acid. It is dark-coloured, very deliquescent, and when heated decomposes into cuprous bromide and bromine. It has been used as an intensifier in photography, for which purpose it is made by mixing equal volumes of $CuSO_4,5H_2O$ (230 g.) and KBr (230 g.) each in 1,000 c.c. H_2O.

Cupric Fluoride, CuF_2, has been prepared by the action of fluorine on copper powder, and also by the action of hydrogen fluoride on cupric oxide at 400°. It forms small white crystals which on exposure to moist air take up water, become blue, and have the composition $CuF_2,2H_2O$.

Cupric Sulphate, $CuSO_4$, is known in the anhydrous form, and also hydrated as $CuSO_4,H_2O$, $CuSO_4,3H_2O$, and

$$CuSO_4,5H_2O,$$

the last being known as *blue vitriol*, which is found in nature as the mineral *chalcanthite*, the most important deposits occurring at Copaquire, Chile, where the rock has been found to contain over 12% of the hydrated salt (E. Walker, Eng. and Min. J. 1903, **75**, 710). The mineral *boothite*, found in California, is reported to be $CuSO_4,7H_2O$ (Schaller, Amer. J. Sci. 1904, [iv], **17**, 191).

Cupric sulphate may be prepared by dissolving metallic copper or preferably the oxide in sulphuric acid. The solution of copper in sulphuric acid is assisted by the presence of nitric acid or sodium nitrate. On a large scale it is made from metallic copper scrap, etc., by heating this material in a reverberatory furnace, throwing in an excess of sulphur, and closing the doors. When combination is complete the doors are opened to admit air and the temperature kept at dull redness to allow the oxidation of the sulphide to sulphate to take place. The mass, while still hot, is discharged into dilute sulphuric acid, allowed to settle, the solution decanted, concentrated and crystallised. The sulphate so produced is of considerable purity. Copper matte, copper glance, and other sulphide ores are similarly treated.

When much iron is present as in most copper ores, and especially in copper pyrites, it is impossible to separate the copper and iron sulphates by crystallisation, because, although copper sulphate crystallises normally with 5 mols of water, it forms, in presence of ferrous sulphate, crystals isomorphous with that salt and containing 7 mols. of water. By carefully adjusting the temperature at which the sulphide is roasted, the iron sulphate may be converted into oxide, while the copper sulphate remains almost unaffected. The iron may be removed by heating the solution of the sulphates to 180° under pressure, when ferrous sulphate crystallises out and may be filtered off. Alternatively, the iron may be separated from the copper by boiling the solution with a little nitric acid, and then removed as oxide by boiling with copper oxide or by boiling with lead peroxide with subsequent addition of a little barium carbonate.

When the sulphate is required for purposes in which the presence of iron is not injurious, such liquors may be at once crystallised out with the formation of crystals containing both iron and copper; much of the *agricultural copper sulphate* is of this class.

Copper containing gold and silver is sometimes treated with sulphuric acid diluted with its own volume of water, the copper being thus dissolved while the silver and gold are left in the residue.

Argentiferous copper ores and mattes are sometimes roasted in reverberatory furnaces, the roasted product being digested with sulphuric acid until little free acid remains. The solution is then decanted from the precipitated lead sulphate, gold, and other insoluble matter, and passed into lead-lined tanks containing plates of copper upon which all the silver and part of the antimony and arsenic present are deposited, while the greater portion of the bismuth is precipitated as a basic sulphate and the iron is reduced to ferrous sulphate. The liquor is then crystallised, the mother liquors being used for treating a fresh quantity of roasted material. Copper sulphate is also obtained in the refining of silver by precipitating it upon plates of copper from its solution as sulphate.

An electrolytic process for the production of copper sulphate consists in using a solution of sodium sulphate and copper electrodes, a current of carbon dioxide being passed through the liquid. Copper is dissolved from the anode as sulphate, while sodium carbonate is produced at the cathode. These react, regenerating sodium sulphate and precipitating copper carbonate, which is collected and dissolved in sulphuric acid (Kroupa, J.S.C.I. 1906, **25**, 78).

A process for preparing cupric sulphate from scrap copper has been patented. In this, the scrap is treated with air in the presence of cupric chloride solution, and the oxychloride sludge so obtained is decomposed with concentrated sulphuric acid, forming copper sulphate crystals and cupric chloride, the latter being returned to the process (B.P. 323115).

Copper sulphate crystallises in large, transparent, blue, doubly oblique, rhombic prisms of sp.gr. 2·28, of the formula $CuSO_4,5H_2O$.

Solubility of copper sulphate in water at different temperatures as g. of $CuSO_4$ in 100 g. solution:

t.	0°	15°	20°	25°	40°
g.	. 12·9	16·1	17·4	18·5	22·8

t.	55°	60°	70°	80°	90°	100°
g.	26·9	28·1	31·4	34·9	38·5	42·4

When heated, it loses 2 mols. of water at 30°, becoming $CuSO_4,3H_2O$, 2 more at 100°, becoming $CuSO_4,H_2O$, and at 260° loses nearly all its water; at 360°, however, a little water (0·04%) is still retained, but by raising the temperature gradually to 400° anhydrous sulphate is obtained (Richards, Proc. Amer. Acad. 1891, **26**, 240).

The salt obtained at 260° is white and hygroscopic, and combines with water with considerable evolution of heat; it combines with water contained in alcohol and other organic liquids with the production of a blue colour, and may be used for detecting the presence of water in these substances, although this test is not very delicate. It has sp.gr. 3·606 and begins to decompose at 361° (Vanjukoff, J. Russ. Phys. Chem. Soc. 1909, **41**, 688). The anhydrous sulphate has also been prepared by heating the pentahydrate at 250° *in vacuo* (F. Krafft, Ber. 1907, **40**, 4770).

Copper sulphate absorbs hydrogen chloride with evolution of heat, forming cupric chloride, and liberating sulphuric acid. It is, therefore, used to remove this impurity from such gases as chlorine, carbon monoxide, carbon dioxide, etc. A similar reaction occurs in solution.

When mixed in solution with molecular proportions of other sulphates, such as those of zinc, magnesium, cadmium, iron, cobalt, manganese, etc., copper sulphate produces well-defined double sulphates which may be rhombic, monoclinic or triclinic, according to the amount of water of crystallisation.

A number of ammino-cupric sulphates have been reported, including $Cu(NH_3)_5SO_4$, $Cu(NH_3)_4SO_4$, $Cu(NH_3)_2SO_4$, and also $Cu(NH_3)_4SO_4,H_2O$. Double sulphates of copper and sodium, potassium, caesium, rubidium, and ammonium are also known, such as: $Na_2Cu(SO_4)_2,2H_2O$, $K_2Cu(SO_4)_2,6H_2O$, $Cs_2Cu(SO_4)_2,6H_2O$, $Rb_2Cu(SO_4)_2,6H_2O$. and $(NH_4)_2Cu(SO_4)_2,6H_2O$.

Ten basic sulphates of copper have been reported in anhydrous or hydrated forms varying in the ratio of CuO to SO_3, such as $5CuO,2SO_3,5H_2O$ and $4CuO,SO_3,4H_2O$ (*v.* Fowles, J.C.S. 1926, 1845).

Copper sulphate is the most important of the copper salts as the large number of copper compounds used in commerce are prepared from this salt. It is largely used in calico-printing, in dyeing, directly or indirectly for the preparation of most pigments containing copper, in electro-plating solutions and in galvanic cells. It is also used as an antiseptic, as a preventative against rot in timber, and in making preparations for protecting plants from various diseases. In agriculture the crude sulphate containing ferrous sulphate is used to prevent "smut" in seeds. For this purpose the seeds are soaked for some hours in a weak solution of the sulphate and are sown within 24 hours.

A 10–20% solution of copper sulphate, preferably mixed with lime, is applied to vines with great benefit. A small quantity is found in the grapes and should be removed, although the tannin and sulphur introduced before fermentation remove it in most cases. Karsten has stated (J.S.C.I. 1896, **15**, 367) that attacks of illness resembling dysentery have been caused by a wine which contained sufficient copper to give a visible deposit on steel in 12 hours. Its presence was due to spraying the vines with a copper salt. An effective wash for vines is prepared by boiling 25 parts sodium carbonate and 25 parts resin in 100 parts water; 2 litres of this solution is diluted with 10 litres of water and added to a solution of 2 kilos of copper sulphate in 50–80 litres of water, the mixture neutralised with sodium carbonate and made up to 100 litres with water (Perraud, Compt. rend. 1898, **127**, 978).

Copper sulphate is used in preparing copper ferricyanide, a solution of which in potassium citrate solution is used as a toning bath for photographs (Ferguson, "Copper Toning," J.S.C.I., 1900, **19**, 465).

Cupric Nitrite, $Cu(NO_2)_2$, is prepared by the double decomposition of cupric sulphate and barium nitrite. It is thus obtained as a bright green solution. It is said to evolve nitric oxide even in the cold, and it absorbs oxygen from the air, being slowly changed to nitrate. According to Râу (J.C.S. 1907, **91**, 1405), when the solution is evaporated under diminished pressure over sulphuric acid, nitric oxide is evolved and the residue, bluish-green in colour, consists of a mixture of nitrite and nitrate, insoluble in water.

A number of double nitrites are known; for example, potassium copper nitrite, $K_3Cu(NO_2)_5$, is obtained by mixing cold saturated solutions of copper sulphate and potassium nitrite, adding methyl alcohol, filtering, and adding ethyl acetate to the clear green filtrate, when long crystals of the salt separate. Rubidium copper nitrite of similar composition may be obtained in like manner (Kurtenacker, Z. anorg. Chem. 1913, **82**, 204). Basic copper nitrites,

$$3Cu(OH)_2,Cu(NO_2)_2 \text{ and } 2Cu(OH)_2,Cu(NO_2)_2,$$

are also known.

Cupric Nitrate, $Cu(NO_3)_2$, may be prepared by dissolving metallic copper, the oxide, or the carbonate in nitric acid. The solution at temperatures above 26° deposits dark-blue crystals containing 3 mols. of water which melt at 114·5° and boil at 170° with evolution of nitric acid and the formation of a green basic salt. This basic salt may also be prepared by boiling the solution of the nitrate with copper or copper hydroxide or with a little alkali. Hydrated crystals containing 9 mols. of water are obtained at low temperatures, −20° to −24°, and crystals containing 6 mols. at temperatures between −20° and +26°.

The anhydrous salt may be obtained by the action of nitric anhydride on the hydrated salt (A. Guntz and M. Martin, Bull. Soc. chim.

1909, [iv], **5**, 1004). By leaving a solution of cupric nitrate in liquid ammonia in contact with copper foil J. Sloan (J. Amer. Chem. Soc. 1910, **32**, 972) obtained crystals of cuprous ammonio nitrate, $CuNO_3,2NH_3$, and by allowing the ammonia to evaporate slowly, anhydrous *cuprous nitrate* is obtained (*v.* F. Ephraim, Ber. 1919, **52**, 236).

Copper Acetate v. Acetic Acid, (Vol. I., p. 54*c*).

Copper Arsenite v. Arsenic (Vol. I., p. 477*d*).

Cupric Phosphate, $Cu_3(PO_4)_2,3H_2O$, is produced by the solution of the carbonate in dilute phosphoric acid and heating the solution to 70°. Caven and Hill found that by boiling this normal phosphate with water or by washing with water at 100° until of constant composition the basic phosphate, $Cu_3(PO_4)_2,CuO,H_2O$, is produced, which compound occurs in nature as the mineral *libethenite* (J.S.C.I. 1897, **16**, 29).

C. O. B.

COPPER GLANCE or *chalcocite v.* Chalcosine.

COPPER PYRITES *v.* Chalcopyrite.

COPRA and **COPRA OIL** *v.* Coconut Oil.

COPROLITES. Concretionary mixtures of calcium phosphate and calcium carbonate, derived from the excrements of certain extinct fishes and reptiles. Used as a fertiliser. Formerly much used in the manufacture of superphosphate of lime.

COPROMESOBILIVIOLIN *v.* Bile Pigments.

COPRONIGRIN *v.* Bile Pigments.

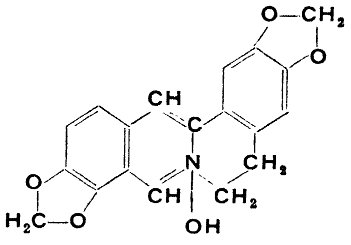
COPROSMA. The bark, and more especially the roots, of *C. grandifolia*, *C. linariifolia*, and *C. areolata* (Fam. Rubiaceæ), which are widely distributed in New Zealand, possess tinctorial property (Aston, New Zealand J. Sci. Tech. 1918, **1**, 3), and being related to madder probably contain either alizarin itself or an allied colouring matter. Thus, an alcoholic extract of *C. grandifolia* is coloured purple by alkali, and becomes yellow on addition of acid. From the acid solution, by means of ether, an orange-yellow crystalline substance can be isolated in small amount.

A. G. P. and E. J. C.

COPTISINE. The roots of *Coptis japonica*, which are used in China and Japan as stomachics, contain besides berberine two other alkaloids, coptisine (I) and worenine. (I) was first isolated by Kitasato (A. 1926, 1160).

The ground roots are extracted with 50% aqueous EtOH, the concentrated extract acidified with sulphuric acid and the precipitated salts extracted with hot EtOH and H_2O; the sulphate of (I) remains undissolved and is thus separated from the two other alkaloids (Kitasato, Amer. Chem. Abstr. 1927, **21**, 2700).

Coptisine is a quaternary base, only slightly soluble in organic solvents, it is best purified by reduction to the racemic tetrahydrocoptisine, m.p. 217–218° (Späth, 227–228°), needles from $EtOH–CHCl_3$, and reoxidation with iodine. For absorption spectra of (I) and that of the tetrahydro derivative, *see* A. 1927, 1095. The salts of (I) are crystalline and highly insoluble: the *iodide*, yellow needles decomposing above 280°; the *chloride*, orange-coloured prisms, does not melt at 300°. By replacing by -OH groups the methylenedioxy groups by means of phloroglucinol, methylating the phenolic -OH groups, and reducing the compound, racemic tetrahydropalmatine was obtained. Kitasato (*l.c.* 1926) therefore attributes to (I) the following constitution:



Coptisine.

I.

it was synthesised by Späth and Posega (Ber. 1929, **62**, [B], 1029) starting from tetrahydropalmatine and from protopine (*l.c.*). Before (I) was found in nature, a base identical with the tetrahydro-derivative had been synthesised by Haworth and Perkin (J.C.S. 1926, 1769). Späth and Julian (Ber. 1931, **64**, [B], 1131) isolated *d*-tetrahydrocoptisine (m.p. 203–204°, $[\alpha]_D^{15}+310^\circ$, in $CHCl_3$) from Austrian corydalis bulbs. Go (Amer. Chem. Abstr. 1931, **25**, 518, or Chem. Zentr. 1931, I, 791) isolated the lævo-compound (m.p. 201–202°, $[\alpha]_D^{17}$ -315°, in $CHCl_3$) from a Corean corydalis. The alkaloid *stylopine*, isolated from *Stylophorum diphyllum* (Fam. Papaveraceæ) by Schlotterbeck and Watkins (Ber. 1902, **35**, 7), is probably identical with tetrahydrocoptisine.

Schl.

COPYING-INK or **INDELIBLE PENCILS.** Originally the pencils sold under these names were intended to be used for copying purposes, and for this reason a water-soluble aniline dyestuff formed an ingredient of the "lead," but the writing done with most of them will yield only faint copies. The term "indelible" is also a misnomer, since the methyl violet, which most of them contain, can be readily bleached.

In addition to the soluble dye, the pigment also contains graphite or kaolin or both. Preparations intended for use in pencils of this type were first patented by Petit (B.P. 4090, 1874), and their composition was described by Viedt (Dingl. poly. J. 1875, **216**, 96). Lehner ("Ink Manufacture," 1902, p. 125) gives the composition of four typical Bavarian pencil pigments, made by Faber, and the table at head of page 360 shows the variation in typical pencils determined by Mitchell (Analyst, 1917, **42**, 1).

The proportion of graphite in the pigment affects the behaviour of the material towards infra-red rays, and enables many of the pigments to be readily distinguished from one another. Pigments in which there is no graphite are transparent in an infra-red photograph (Mitchell, Analyst, 1935, **60**, 459).

Origin.	Moisture.	Residue insol. in water or alcohol.	Dyestuff.	Loss on ignition (graphite, etc.).	Ash (kaolin, etc.).
	%	%	%	%	%
American	2·35	76·45	21·20	27·09	47·36
,,	7·48	51·53	40·99	25·48	31·92
,,	2·30	60·89	36·81	56·84	4·05
,,	3·75	63·95	32·30	13·90	50·05
Austrian	3·56	47·14	49·94	44·14	3·00
British	2·72	65·48	31·80	62·08	3·40
,,	4·53	73·05	22·42	69·17	3·88
German	3·72	64·48	31·80	11·86	52·86
,,	6·33	59·83	33·84	7·61	52·22
,,	3·83	57·59	38·58	40·01	17·58

Copying ink pencils containing a large proportion of alumina tend to be more indelible than those in which the pigment consists only of graphite and dyestuff. In this country only the violet pencils are in demand, for blue and red pencils usually contain an insoluble pigment instead of a dye; the composition of the pigments of typical coloured pencils was determined by Mitchell (Analyst, 1922, **47**, 385). A simple charring test, in which the graphite of a copying ink pencil is left on the coherent ash of the paper, enables the sequence of two intersecting strokes made with a copying-ink pencil of the graphite type to be determined (Mitchell, Analyst, 1925, **50**, 178).

C. A. M.

CORACAN *v.* Cereals, (Vol. II, p. 488*d*).

CORAL is the calcareous substance secreted by several different organisms. The best known of these belong to the *Coelenterates* and include: (1) some Hydrozoa known as *Millepores*, common on tropical coral reefs, (2) a large number of Actinozoa (Anthozoa), which include the commonest reef-building corals and the precious coral of industry. The term coral is also loosely applied to (3) some of the Polyzoa (known as sea-mats or zoophytes) which have coral-like forms and are the chief constituent of the Tertiary deposit known as the "Coralline Crag"; (4) some shallow water Foraminifera, very primitive shell-bearing animals which form an important percentage of the sand of coral reefs; (5) certain sea-weeds (*Nullipores* or *Calcareous Algæ*) which have a calcareous skeleton and are also common on coral reefs.

A large number of analyses of coral are given by F. W. Clarke and W. C. Wheeler (U.S. Geol. Surv., Prof. Paper 124, 1922), and a selection of these is given in the table:

Percentage Composition of Coral.

	CaO	MgO	SiO_2	Loss on ignition.
Hydrozoa—				
Millepora alcicornis	52·50	0·43	0·23	44·77
Actinozoa—				
Porites astreoides	53·84	0·18	0·02	44·98
Madrepora prolifera	53·48	0·06	0·19	44·50
Favia fragum	53·69	0·18	0·28	44·44
Maeandra labyrinthiformis	53·71	0·26	—	45·10
Polyzoa—				
Flustra membranacea	30·81	2·06	3·00	61·45
Foraminifera—				
Orbitolites marginalis	48·92	4·93	0·03	45·20
Algæ—				
Lithothamnium	48·00	4·78	0·41	45·41

The precious coral of industry is chiefly *Corallium rubrum*. It is obtained in depths between 90 and 900 ft. in the Mediterranean. The richest fishery is on the banks off the Algerian and Tunisian coasts and also off the coast of Sicily. Black coral comes from Jidda in the Red Sea, and white and red (Morro) coral of good quality comes from Japanese waters. All are used in the manufacture of jewellery. The composition of precious coral is given by G. F. Kunz (in D. K. Tressler, "Marine Products of Commerce," 1923) as shown in table opposite.

	Red coral.	Black coral.
Calcium carbonate . . .	86·974	85·801
Magnesium carbonate . .	6·804	6·770
Calcium sulphate . . .	1·271	1·400
Ferrous oxide	1·720	0·800
Organic matter	1·350	3·070
Water	0·550	0·600
Phosphorus, silica, etc. . .	1·331	1·559

The colour of black coral is said to be due to the organic matter, while some workers have said that the colour of the red coral is due to iron. The red colour, however, is destroyed on ignition, so that presumably it is an organic compound formed by the polyps. The specific gravity of precious coral is close to that of calcite, varying from 2·6 to 2·7, but its hardness ($3\frac{3}{4}$) is a little greater. The low hardness facilitates carving and turning and, though it does not take a fine polish, the beauty of hue makes up for this and it wears well. The colour of red coral varies from crimson to rose, the latter being the rarest and therefore most prized.

Although the analyses in the tables give the composition of some of the more important corals, it is known that important changes in the composition take place at comparatively shallow depths in coral reefs. The calcium carbonate is largely replaced by magnesium carbonate, which may rise as high as 38%. This imperfectly understood phenomenon is known as *dolomitisation*, and has been most closely studied in the borings from the Atoll of Funafuti (J. W. Judd, Phil. Trans. 1904, " The Atoll of Funafuti," pp. 362–389; E. W. Skeats, Amer. J. Sci. 1918, **45**, 185). It was found that down to the depth of 637 ft. dolomitisation had only occurred to a slight extent, the magnesium carbonate never exceeding 16%; but the lower portions of the bore were very rich in magnesium carbonate, containing from 30 to 43%. Different degrees of dolomitisation have been found in other bores in different reefs.

Sandy islands on coral reefs are the home of innumerable sea-birds, and their excreta replace the carbonate in the coral by phosphates. This guano may be, as is the case on the coral reef known as Christmas Island, of commercial importance. The deposit may contain as much as 38·5% of phosphoric acid.

(For an account of the distribution, structure, and formation of coral reefs, *see* J. D. Dana, " Corals and Coral Islands "; C. Darwin, " Coral-Reefs "; W. M. Davis, " The Coral Reef Problem.")

A. P. O.

CORAL-ORE *v.* CINNABAR.

CORAMINE (CIBA). Pyridine β-carboxydiethylamide. Used as a cardiac stimulant.

CORDEAU DETONANT or DETONATING FUZE. Several varieties of this fuze, which is used for firing a number of explosive charges simultaneously, have been manufactured, but the type most largely used at present consists of a narrow lead tube filled with trinitrotoluene. It is fired by means of an ordinary detonator and safety fuze or by means of an electric detonator.

H. S.

CORDIALS AND LIQUEURS. These are spirituous mixtures usually sweetened and flavoured with essences obtained from herbs, spices or other substances, and often strongly coloured. They are manufactured and used to a much greater extent in France and other Continental countries than in the United Kingdom, and although there is no essential difference between them, the term " cordials " is by many restricted to British and American preparations, and " liqueurs " to those originating elsewhere.

The spirit in the best quality of liqueur is derived from the grape, but grain, molasses or other spirit is frequently employed, especially in cordials. In the case of citrus cordials the spirit used is often prepared by fermentation of the juice of the fruit after the addition of sugar. Whatever the origin of the spirit it should be highly rectified, and unless obtained from the basic fruit it should be neutral in character, so as not to impair the flavour of the finished product. The alcoholic strength of cordials and liqueurs varies greatly, but, on the average, they contain from 30 to 40% of alcohol, approximately equivalent to 50 to 70% of proof spirit.

The principal flavouring ingredients employed fall into three classes. Those used solely on account of their essential oils include aniseed, bitter almonds, caraway, juniper berries, mint, lemon-peel and orange blossom. Those valued for their bitter principles as well as their essential oils include cinnamon, cloves, curacoa apples (a kind of orange), gentian, ginger, orange-peel, sweet calamus, wormwood and vanilla. The third class of flavouring consists of fruits, such as cherries, pineapples, raspberries and strawberries. The flavourings are prepared for use either by digesting with alcohol and distilling the mixture to obtain an essence, filtering the alcoholic extract to form a tincture, or by expressing and clearing the juice of fruits. Those for citrus cordials are sometimes prepared by expressing the oil from the peel, the juice of the fruit being fermented, after the addition of sugar, to give the necessary spirit. Artificial essences simulating the above flavourings are frequently employed, but their use in beverages is questionable, since it is possible that their physiological action differs from that of the natural flavouring substances which they are intended to imitate.

The sweetening material used may be sugar, honey or glycerol. In the case of the former it should be commercially pure and, before addition to the preparation, is dissolved in water to form a syrup.

The colouring matters most commonly used are: *red*, aniline red, brazilwood, cochineal, cudbear, and sandalwood; *yellow*, saffron and turmeric; *blue*, indigo; *green*, chlorophyll; *violet*, aniline violet; *brown*, burnt sugar or caramel.

F. G. H. T.

CORDITE. This smokeless powder, in various modifications, is the principal British Service propellant. It is usually in cord-like form, but for special purposes it is made into tubes with single or multiple perforations, and is sometimes used in the form of flakes made by slicing the cords.

Composition.—Ordinary cordite is essentially a mixture of guncotton and nitroglycerin, gelatinised by means of acetone, together with a small quantity of mineral jelly (soft paraffin), the whole being thoroughly incorporated. The mineral jelly was originally added to prevent fouling of the rifle, but it was found to diminish erosion by acting as a cooling agent, to improve the regularity of the burning, and also to act as a waterproofing agent. The unsaturated hydrocarbons such as olefines and naphthenes present in the mineral jelly, by combining with the products of decomposition of the nitro-bodies, tend to stabilise the cordite. Furthermore, the mineral jelly to a certain extent protects the nitroglycerin and nitrocotton from atmospheric influences.

The original cordite (Cordite, Mark I) was composed of nitroglycerin 58%, guncotton 37%, and mineral jelly 5%. The guncotton had a nitrogen content of 12·8 to 13·1% and from about 10–12% was soluble in ether-alcohol. Owing to its high nitroglycerin content this cordite had a high temperature of explosion, and produced considerable erosion in guns of large calibre. In 1901 a modified form was produced, known as Cordite M.D. In this variety the percentage of nitroglycerin was considerably reduced, the composition being nitroglycerin 30%, guncotton 65%, and mineral jelly 5%.

Manufacture.—The guncotton containing about 30% of moisture is dried in a stove by a current of hot air until the moisture is reduced to about 0·5%. The cooled, dried guncotton is weighed out into rubber-lined canvas bags and then taken to the nitroglycerin filtering house, where the requisite quantity of nitroglycerin is measured out through a rubber tube on to the guncotton. The bag is then carried to the mixing house where the contents are mixed by hand on a lead table which is perforated at one end with ½-in. holes through which the material is rubbed into the bag below. The product at this stage is known as "Cordite Paste." To effect incorporation, part of the acetone is first poured into a kneading machine of the Werner Pfleider type, the machine started, and the cordite paste, together with the remainder of the acetone, about 56% of the weight of the guncotton in all, gradually added. The mixture is covered to prevent loss of acetone and the mixing continued for 3½ hours.

At the end of this time the charge of mineral jelly is added and the machine run for a further 3½ hours. During these operations the acetone gradually dissolves the guncotton and nitroglycerin and thoroughly incorporates them with the mineral jelly. The resulting product is known as "Cordite Dough." The stiff dough becomes somewhat heated during the mixing, but the temperature is not allowed to exceed 40°C., and is controlled by the water jacket with which the machine is provided. The dough is then conveyed in bags to the press house, where it is squirted or pressed, by plungers working in cylindrical moulds, through a die with one or more holes according to the diameter of the cord required. A perforated plate supporting a fine wire gauze is placed above the die to retain mechanical impurities. Pressing into tubes is effected by means of a die with a pin in the centre, but when small sizes are being pressed considerable trouble is experienced through a partial vacuum being formed and consequent collapse of the tube. This can be avoided by the use of a hollow pin with communication to the outer air.

The smaller sized cords are wound automatically on to reels as they leave the die, the larger sizes are cut into the required lengths.

For drying, the reels of cordite and the larger sizes on trays are placed on open racks in stoves heated by steam pipes or by a current of air at a temperature of about 40°C. For the smallest sizes no stove heating is required in the summer; all that is necessary is to keep the cordite at a temperature of about 15°C. for a few days. The time required for drying the large sizes at 40°C. varies, according to the diameter of the cord, from 2 to 15 days. Cordite M.D. requires a much longer time for drying than the Mark I type, several months being necessary for the largest sizes.

The drying process removes moisture and the greater part of the acetone, of which about 15% remains in the pressed cordite. Since the amount of acetone present is appreciable, arrangements are made for its recovery. One of the recovery processes is Robertson and Rintoul's (B.P. 25994, 1901) and consists in passing the acetone-impregnated air from the stoves through a series of towers down which a 30% solution of sodium bisulphite is trickling. The acetone combines with the bisulphite and when the solution is nearly saturated it is transferred to a still where after the addition of a little sodium carbonate the liquor is distilled. The acetone thus recovered is purified by fractionation.

After drying is complete, different batches of cordite are thoroughly blended in order to obtain uniformity of composition and ballistic properties. This is effected in the case of the smaller sizes by rewinding several reels simultaneously on to a single drum. The larger sizes are blended by hand, the sticks from the drying stove trays being placed in boxes and the contents of these mixed by combining a few from each box, the operation being repeated. Before blending, the sticks are carefully examined and any which are badly distorted or contain specks of foreign matter are discarded.

Properties.—Cordite varies in colour from light to dark brown. The thin cords of the Mark I material are flexible, but the larger sizes break easily when bent. Cordite M.D. is considerably harder and more brittle and is difficult to cut with a knife.

The specific gravity of Cordite, Mark I, is about 1·56–1·57, that of Cordite M.D. being 1·58–1·59.

Cordite is water repellent and can be kept under water, salt or fresh, for some time without its explosive properties being affected. Even when fired wet in a gun the ballistics only fall off to the extent due to the evaporation of the water. On prolonged cold storage the nitroglycerin exudes slightly, but is gradually re-adsorbed when the temperature rises.

Cordite does not ignite very readily, but once ignited burns relatively slowly with a strong yellowish flame which is practically smokeless. A stick becomes pointed at the end as it burns and the flame can be extinguished by blowing strongly on it. A considerable bulk of cordite can be burnt in the open without any explosion. It only burns explosively when strongly confined. If ignition of cordite confined in wooden boxes occurs, the material does not explode, but burns quietly, although the boxes may be burst open by the escaping gases.

Owing to the difficulty in ignition of cordite a stronger cap of different composition is necessary to ignite the fine cordite in small arm ammunition than was required for black powder, and to ensure the ignition of the larger sizes the charge of cordite has to be primed with an ordinary black powder or guncotton primer which passes on the flash of the igniting tube to the charge.

Cordite is very insensitive to shock and cannot be exploded by the passage through it of a rifle bullet. Exhaustive trials under very varied climatic conditions have shown that the ballistic stability of cordite is of a high order. The ballistic power is very nearly four times that of black powder owing to the increased volume of gases liberated per unit weight and the high temperature of the explosion.

Cordite can give a pressure of more than 120 tons per sq. in. as compared with the maximum of 43 tons obtainable with black powder, but in practice the pressure in the gun does not nearly attain this figure owing to the relatively large size of the gun barrel compared with the volume of the cordite.

The ballistic properties of cordite are more influenced by temperature than is the case with black powder, the pressure developed and the velocity of the shot being greater at increased temperatures, but not to the extent of seriously modifying the shooting under Service conditions. Cordite burns more quickly under high pressures than low and the smaller the size of cord the more rapid is the combustion. The pressure due to cordite is more gradually developed in the gun than is the case with black powder and is better sustained.

Numerous analyses of the products of explosion of cordite have been published by Noble (Proc. Roy. Soc. 1905, **76**, 381). The following results were obtained by exploding the powders in a calorimetric bomb, the loading density being 0·05 :

	Cordite, Mark I.	Cordite M.D.
Vol. permanent gas ml. per g.	678·0	781·8
Vol. total gas ml. per g.	877·8	955·4
Composition of permanent gas :	%	%
Carbon dioxide	27·15	18·15
Carbon monoxide	34·35	42·60
Hydrogen	17·50	23·15
Methane	0·30	0·35
Nitrogen	20·70	15·75
	100·0	100·0
Composition of total gas :		
Carbon dioxide	20·97	14·85
Carbon monoxide	26·53	34·87
Hydrogen	13·52	18·95
Methane	0·23	0·29
Nitrogen	15·99	12·89
Water	22·76	18·15
	100·0	100·0
Pressure tons/sq. in.	2·9	2·7
Heat evolved (water liquid) cal. per kg.	1,272	1,036
Temperature of explosion (calculated)	5,151°C.	4,056°C.

The temperatures being calculated with very low values for the specific heats, are consequently high and have only relative value. The temperature of explosion as determined by Robertson was found to be 2,663°C. for Mark I, and 2,374°C. for Cordite M.D.

The larger volume of gaseous products and the lower temperature of explosion explain why the erosive effect of Cordite M.D. is so much less than that of Cordite, Mark I.

The erosive effects of cordite are less than those of black powder and of a different character. With the latter, the bore of the gun is pitted by the corrosive action of the products of combustion, whilst with the former only the surface near the powder chamber is smoothly washed away by the passage of the hot gases between the projectile and the bore before the inertia of the shot is overcome.

Cordite M.D. gives far less flame than Cordite, Mark I, when used in rifles or machine guns.

Analysis of Cordite Mark I and M.D.—*Volatile Matter.* 5 g. of the ground cordite are heated for 3 hours on a boiling water plate in an aluminium dish covered with a glass cone, both of specified dimensions (*see* Marshall, J.S.C.I. 1904, **23**, 154).

Guncotton.—2 g. of the ground cordite are extracted with ether for 2½ hours in a weighed Soxhlet thimble. The residue is dried at 82°C. until constant in weight.

Mineral Jelly.—The ether extract is evaporated to dryness and the nitroglycerin is removed by treatment with methyl alcohol. The alcoholic solution is filtered and any mineral jelly which has been transferred to the filter is washed back into the flask by means of ether. The ether is distilled off and the residue dried in the boiling water oven, any traces of nitroglycerin vapour being removed by a current of air. The drying operation is continued until the mineral jelly is of constant weight.

Nitroglycerin.—This is usually estimated by difference.

Abel Heat Test.—This is the British official heat test which is applied to nitro explosives generally. The principle of the test is to note the time required to produce a standard tint on a potassium iodide starch paper when the explosive is heated under specified conditions. The explosive is weighed out into test tubes about 5¼ to 5½ inches long having a capacity of 20 to 22 ml. when filled to a height of 5 inches. They are provided with an india-rubber stopper fitted with a glass rod terminating in a platinum wire hook. On the hook is suspended a test paper about 10×20 mm. in area, the upper half of which is moistened with a mixture of equal parts of glycerol and water. The test tubes are placed to a depth of 3 inches below the cover of a water bath, the temperature of which is carefully regulated at the specified temperature (usually 160–180°F.). The water bath is a spherical copper vessel about 8 inches in diameter fitted with a cover having a number of circular holes (usually six) and fitted on the underside with clips to take the tubes. The bath is fitted with a thermometer, the bulb dipping 2¼ inches into the bath, and usually some form of temperature regulator. The test is complete when the faint brown line, which appears at the junction of the wet and dry parts of the test paper which is adjusted to be ⅝ of an inch above the cover, is equal in tint to the brown line on a standard tint paper.

Cordite R.D.B.—Owing to the shortage of acetone during the War a further modification known as Cordite R.D.B. was introduced. This variety contained nitrocotton 52%, nitroglycerin 42%, and mineral jelly 6%, the nitrocotton having a comparatively low nitrogen content (12–12·2%) and capable of being gelatinised by means of ether-alcohol.

This cordite was designed to give similar ballistics to cordite M.D., and in practice it was found to be in no way inferior to the latter in this respect.

In the case of Cordite R.D.B. the solvents were originally recovered by absorption in sulphuric acid. The Daniel and Brégeat process (B.P. 127309) takes advantage of the property of phenol and its homologues such as cresol of absorbing ether and alcohol, and this method of solvent recovery was employed at various factories during the War with very satisfactory results, about 50% of the total solvent being recovered.

H. S.

CORDYLITE or BARIUM-PARISITE. Carbonate and fluoride of cerium-metals and barium, $(CeF)_2Ba(CO_3)_3$, containing Ce_2O_3 23·72% and $(La,Di)_2O_3$ 25·67%. It occurs as small, pale wax-yellow, club-shaped hexagonal crystals in syenite-pegmatite at Narsarsuk near Julianehaab in south Greenland; sp.gr. 4·31. It is isomorphous with, and closely related to, parisite.

L. J. S.

CORÉOPSINE POUR CUIR *v.* Acridine Dyestuffs (Vol. I, p. 133).

CORIANDER.—The dried fruit (seed) of *Coriandrum sativum* Linn. (Fam. Umbelliferæ), indigenous to Italy, but cultivated throughout Europe, especially in Russia. The plant is an herbaceous annual with an erect and branching stem rising to about 2 ft. in height. It bears white or pinkish flowers in June and the fruit ripens in August, the fruits being in distinct contrast to all those other umbelliferous plants employed for flavouring purposes in that they are globular with a diameter about twice the size of mustard seed. The plant is abnormal also in that any part of the fresh plant, when bruised, emits a fœtid odour, whilst the fruit becomes fragrant on drying. The plant is cut and threshed when the fruit is ripe. The fruit is composed of two pale yellowish-brown sub-globular mericarps united at their margins, 2 to 4 mm. in diameter, and in cross-section reveals its similarity to other umbelliferous fruits, in that each mericarp possesses five primary wavy ridges but with four more prominent, straight, secondary ridges. Vittæ, or oil ducts, are only present on the commissural sides of the ripe fruit, two in each mericarp; there are many others in the unripe fruit, but these disappear as it develops. The taste is sweet and aromatic, and the fruits are largely used for flavouring purposes, especially in curry powder, and as a carminative.

Microscopic Appearance.—During ripening the outer pericarp is almost entirely discarded, so that stomata are seldom observed, and the chief diagnostic features are the pitted fusiform cells of the lignified sclerenchyma, which are only present on the outer surface of the mericarp. These are five to ten layers deep and cross each other. The vittæ are 300 to 400μ in diameter. The inner mesocarp merges into the endosperm and consists of thick-walled parenchymatous cells, containing aleurone grains, fixed oil, and minute rosettes of calcium oxalate.

Chemical Composition.—C. Arragon (Ann. Falsif. 1915, **8**, 345) gives the following composition of a sample of coriander fruit:

	%
Water	9·2
Ash	7·01
Fat	20·6
Essential oil . . .	2·2
Protein	14·2
Fibre	24·7
Starch and reducing substances . . .	21·2

All the figures other than water are on the dry material.

The principal constituent is the essential oil, which varies from 0·4 to 1·0%, the figure obtained by Arragon (*supra*) is high, and the best method of determination is probably that of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435). The powdered fruit is mixed with brine, distilled, and the vapours passed through the top of a condenser into a graduated tube, in which the oil is collected whilst the condensed water is returned to the distillation flask. An air inlet or outlet is provided by means of a side tube below the condenser but above the graduated tube. These authors found that the yield of oil is increased slightly by powdering the fruits before distillation, but that the powdered drug loses oil on storage. They found from 0·25 to 0·40% of oil in commercially powdered fruit. For further details of the oil, *see* Coriander, Essential Oil of.

Standards.—The "British Pharmacopœia" requires that coriander shall contain not more than 2% of foreign organic matter; ash not more than 7%; acid-insoluble ash not more than 1%.

T. McL.

CORIANDER, ESSENTIAL OIL OF. The oil distilled from the ripe fruits of *Coriandrum sativum* Linn. (Fam. Umbelliferæ), a native of central Europe and cultivated in Morocco, Thuringia, Russia and India. It is also grown in Cyprus. Other parts of the plant yield an inferior oil having a bug-like odour.

Constituents.—The chief odorous constituent is *d*-linalool, formerly known as *coriandrol*. The terpenes present are α-pinene, β-pinene, *p*-cymene, dipentene, terpinolene, terpinene, and phellandrene. It also contains traces of borneol, geraniol, *n*-decylic aldehyde, and esters of acetic and decylic acids.

Characters.—A colourless or pale yellow oil, sp.gr. 0·870–0·885, optical rotation +8° to +13°, ref. ind. 1·456 to 1·478. Soluble in 3 volumes of 70% alcohol. Alcohols determined by formylation 60 to 80%. The determination of linalool cannot be made by the acetylation process owing to the decomposition of the alcohol.

This oil is used largely in the manufacture of liqueurs and in the chocolate industry. It is also employed in medicine as a carminative and flavouring agent.

C. T. B.

CORIANDROL *v.* Coriander, Essential Oil of.

CORINDITE is the name given to a refractory and abrasive material which has been claimed as a "new product." In 1914 a French engineer, Noel Lecesne, patented a process of fusing bauxite economically. A mixture of 3 parts crude bauxite, as quarried, and 1 part of anthracite is heated in a cupola oven and air blown into the lower portion. The bauxite is reduced, with the formation of aluminium carbide, which in the presence of excess of air is almost entirely oxidised to alumina, the heat of the reaction being such that the mass fuses in successive layers. On cooling, a vesicular mass is left, through which an immense number of small crystals of fused alumina are disseminated (F.P. 471513; J.S.C.I. 1915, **34**, 356). There are two varieties of French bauxites, white and red; the former when fused has a melting-point of 1,950°C., the latter resembles emery and is a powerful abrasive. It is stated that Irish bauxite (Larne), white and low in Al_2O_3, hitherto of little commercial value, gave a product equal to that obtained from French material. The crushed corindite is mixed with finely-ground refractory binders, such as bauxite, kaolinitic clay, etc., moistened and moulded into shapes which have a very low air-shrinkage. The dried bricks are fired at 1,350° to 1,400°C. and up to 1,750°C. show very little variation in volume. The porosity varies with the mechanical composition of the mixtures and ranges from 9 to 12%. Lime, magnesia, etc., are not suitable binders as they lower the refractoriness. Corindite articles also have great resistance to depreciation and have been recommended for rotary cement kilns, heavy oil and gas engines, coke-ovens, etc. (Bigot, Trans. Ceram. Soc. XVIII, 267; La Céramique, 1917, **20**, 41; Eng. and Min. J. 1917, **104**, 417; J.S.C.I. 1917, **36**, 1094).

W. C. H.

CORINTH RK (INDANTHRENE GREY K) *v.* Anthraquinone Dyestuffs Vol. I, p. 420*a*.

CORIOFLAVINE. An acridine dyestuff *v.* Vol. I, p. 133*c*.

CORIPHOSPHINS are acridine dyestuffs *v.* Vol. I, p. 132*b*.

CORK. Cork is derived from the bark of two evergreen species of oak, *Quercus Suber* Linn., sometimes regarded as a variety of *Q. Ilex* (holm-oak) rather than as a distinct species, and *Q. occidentalis* Gay. The former yields the best cork, and grows chiefly in countries bordering the Mediterranean, whilst the latter occurs on the Atlantic seaboard of Portugal, Spain, and France.

The chief sources of supply of cork are Spain and Portugal, which together produce about four-fifths of the world's output. Algeria and Tunis also contribute to the supply, and smaller quantities are obtained in Southern France, Corsica, Sardinia and Sicily.

The cork tree is from 20 to 60 ft. high, 3 to 4 ft. in diameter, and attains an age of 150 or sometimes even 200 years. It thrives best on sandy or granitic soils. The quality of the bark depends on the nature of the soil, trees on poor soils producing bark of fine texture whilst those on rich soils give a thicker, coarser and spongy bark. The cork is developed in the cortex by the activity of a meristematic layer of tissue, the phellogen or cork cambium.

Barking the Trees.—This operation requires great care, as on it depend the life of the tree and the regularity of the cork slabs produced. Two cuts are made round the stem—one a little above the ground and the other just beneath the spring of the main branches. Three or four vertical cuts are made and the bark is stripped off by inserting beneath it the wedge-shaped shaft of the implement used to make the incisions. Care must be taken not to injure the phellogen. The first stripping is effected when the tree is 15–20 years old. The product, termed "virgin cork," is rough, uneven, and woody in texture, and is of little value as it is not sufficiently elastic for use as bottle corks. It was formerly used for the production of Spanish black and for ornamental rustic work, but of late years it has been employed in the form of ground cork for insulating purposes and for linoleum manufacture. After 8–10 years a further layer of cork is removed from the trees; this, known as "secondary bark," is of much better quality than the virgin cork but not so fine in texture as the third and later strippings, which are collected at further intervals of 8–10 years.

After the slabs of cork have been taken from the trees, they are stacked and weighted with heavy stones to flatten them. The cork is then immersed for 5 or 6 minutes in a tank of boiling water which causes it to swell and improves its softness and elasticity; the water also removes tannin and other soluble matter. In Spain the cork is sometimes passed through a fire, whereby it is superficially charred, and is supposed to acquire special qualities. The slabs are finally hydraulically compressed and baled for the market.

Physical Properties and Uses.—The chief characteristics of cork that render it peculiarly suitable for the various uses to which it is applied are its low sp.gr. (average about 0·16), its compressibility, elasticity and impermeability to both air and water, and its low thermal conductivity. In addition to its extensive employment in bungs and stoppers for bottles and other vessels containing liquids, it is used in making mats, soles for shoes, linings, artificial limbs and many other articles.

Waste cork is granulated by suitable machinery, and then ground to powder. The finest dust is used in conjunction with linseed oil for the manufacture of linoleum and other floor coverings. The most important use of cork waste, however, is as insulating material.

Many methods have been devised for the manufacture of moulded slabs in which use has been made of various binding materials, such as gluten, casein, tar, pitch, and mixtures of glue with oily and resinous substances. Another method of making cork slabs or boards is carried out by placing the ground waste in iron moulds, subjecting it to heavy pressure and heating it in an oven at about 450–500°. This treatment effects the cohesion of the cork particles without the addition of any extraneous material, and the product is termed "baked slab cork."

Chemistry of Cork.—Cork consists essentially of suberin, but contains about 2·9% of cerin or cork wax (m.p. 250°). According to Karrer, Peyer, and Zega (Helv. Chim. Acta, 1922, **5**, 853) cellulose is present to the extent of 1·6–3·0%. The composition has been studied by Zetzsche and his co-workers (Helv. Chim. Acta, 1927, **10**, 346; 1928, **11**, 272; 1931, **14**, 632), Kügler (Arch. Pharm. 1884, 217), Gilson (*ibid.* 1890, 690), Hy. Ingle (J.S.C.I. 1904, 1197), M. von Schmidt (Monatsh. 1904, **25**, 277, 302; 1910, **31**, 347).

Gilson saponified cork from *Q. Suber* with 3% alcoholic potash, and isolated from the filtrate 44% of fatty acids, consisting of: "phellonic acid," $C_{22}H_{43}O_3$, m.p. 102°, a monobasic acid giving a violet colour with zinc chloride-iodine solution, yield 8%; "suberinic acid," $C_{17}H_{30}O_3$, a semi-fluid sticky substance, yield 36%; and a small amount of "phloionic acid," $C_{22}H_{44}O_8$, m.p. 62–63°. He considered suberin to be a mixture of complex esters and possibly condensation products of different acids. Scurti and Tomassi (Gazzetta, 1916, **46**, [ii], 159) have found that phellonic acid is identical with α-hydroxybehenic acid and that suberinic acid is either ricinoleic acid or an isomeride of it.

Schmidt expressed the view that suberin was partly composed of glycerides, although previously only small quantities of glycerol had been found among the degradation products of cork. In order to account for the excess of acids above the amount required to form the glycerides, he suggested that they were present as anhydrides or polymerides. He was further of opinion that young cork contains glycerides only, which, under the influence of air, light, and probably also of enzymes, suffer hydrolysis, the glycerol being partly oxidised to carbon dioxide and water whilst the fatty acids partly polymerise and partly form anhydrides. Zetzsche considers that suberin consists of high molecular polymerides of unsaturated acids, mainly hydroxy-acids, and regards Schmidt's hypothesis that they are present as anhydrides as unlikely. On hydrolysing pure cork (prepared by the action of boiling aqueous sodium sulphite on crude cork) with alcoholic sodium hydroxide, Zetzsche and Sonderegger found that sodium phellonate (α-hydroxybehenate) separated and that the acids from the other sodium salts were *phloionic, corticinic, suberic, suberolic,* and *phloionolic,* the total acid fraction amounting to 28–36% of the crude cork.

When treated with strong nitric acid, cork is converted into suberic acid, oxalic acid, and other products. It is charred by strong sulphuric acid, but is little affected by hydrochloric acid. Chlorine, bromine, and iodine cause cork to shrink, the two former first bleaching it. On ignition it swells and forms a charcoal known as Spanish black.

E. G.

CORNISH STONE *v.* China-Stone.

CORN OIL or MAIZE OIL *v.* Cereals, Maize.

CORNUITE *v.* Chrysocolla.

CORONILLIN, $C_{23}H_{33}O_{10}$, $[\alpha]_D$ −17·6°, the glycoside of the seeds of *Coronilla scorpioïdes* and *C. varia*, is hydrolysed to glucose and an aglucone, $C_{17}H_{23}O_5$. It is not attacked by emulsin, although split by one of the enzymes in *Aspergillus niger.* The glycoside is very toxic and has a moderate cardiac and low diuretic action (Tanret, Compt. rend. 1934, **198**, 1637).

E. F. A.

COROZO. Vegetable ivory, the seeds of the *Phytelephas macrocarpa.*

CORROSION OF METALS. General.—Corrosion is a chemical process which results in the wastage or deterioration of metals, and may thus be distinguished from erosion, which denotes a wearing away by mechanical agencies. Corrosion may occur either as a "direct chemical" or as an "electrochemical" attack, but these are phases of the same fundamental process, the essential feature of which is a decrease in the free energy of the system. Conditions favouring the first type are more often afforded by contact with gases or moisture-containing atmospheres, whilst immersion in liquids favours the production of electrical currents and hence the second type of attack; but this is by no means a general rule, and the distinction between atmospheric and immersed corrosion is usually dictated by other factors to be considered later.

The end product of a corrosion process is often a compound which is found in nature as a mineral. Thus, copper exposed for many years to an inland atmosphere becomes covered with a coating of basic sulphate which is similar to the mineral *brochantite* and iron or steel when totally immersed in certain waters and salt solutions, yields, after long periods, hard deposits of hydrated ferric oxide which closely resemble *goethite.* Corrosion is thus the reversion of a metal from a metastable metallic state to a stable oxidised state; metals which occur as such in nature, *e.g.* gold, do so because they are corroded only by reagents not commonly found in nature, or because, as in the case of copper, they occur "native" in certain strata from which oxygen and salt solutions are largely excluded. Structurally, corrosion may affect a metal in several different ways: (1) The changes are confined essentially to the surface, on which the corrosion product may either accumulate or be removed in solution or otherwise, leaving a *residue of unaltered metal.* (2) The changes at the surface are accompanied by more or less *intercrystalline penetration*; this "intercrystalline corrosion" leads to brittleness or weakness in the underlying metal although the bulk of it may have undergone no change. (3) The changes are definitely not confined to the surface, but extend *throughout the mass of the material* (" metasomatic change "). In extreme cases a complete change of composition may be effected whilst the article retains exactly its external shape. Examples are provided by the " graphitisation " of cast iron and the so-called " dezincification " of brass, reference to each of which will be made later (*see* " Corrosion by Sea-water " p. 381 and " Corrosion by Soils," p. 384).

Methods for protection against corrosion should theoretically exclude entirely all substances which promote reversion to the stable condition. These vary with the metal but usually include oxygen, as gas or in solution, and water-soluble substances; these are difficult to exclude entirely, and advantage may then be taken of the so-called " self-stifling " processes which are described later. A detailed knowledge of the mechanism of corrosion may often provide the key to corrosion protection processes, and an immense amount of work has been done to elucidate this mechanism.

It is convenient to divide the consideration of this subject into two parts, one dealing with metals wholly or partially immersed in liquids, and the other with metals exposed to gas atmospheres from which liquid water may or may not be deposited; a justification for this procedure is that the factors which control the rates of corrosion in the two sets of conditions are in general different. (By " controlling factor " is understood that factor which, under the particular conditions, has the greatest influence in *restricting* the rate of corrosion.) For example, it is characteristic of many kinds of atmospheric corrosion that oxygen is present in excess at or close to the metal surface and consequently the rate of corrosion is usually controlled by some factor other than the rate of oxygen supply, *e.g.* by the humidity, the presence of other gases such as sulphur dioxide, or the nature of the initially formed corrosion product; on the other hand, when a metal is immersed in a salt solution the rate of corrosion is often dependent largely upon the rate at which oxygen reaches the metal surface or its immediate neighbourhood. It is for this reason that differences both in composition of the metal and also in climate give rise, in general, to much greater differences in behaviour on complete exposure to the atmosphere than under conditions of complete immersion in the sea. This is illustrated in Fig. 1, taken from a paper by Robert Hadfield and S. A. Main (J. Inst. Civil Eng. 1936, 25) in which the authors survey the results of 5-year field tests of the Institution of Civil Engineers. It is apparent from this diagram that maximum differences are exhibited by the aerial tests, maximum agreement by the complete immersion tests, whilst the tests representing " half-tide " conditions occupy an intermediate position.

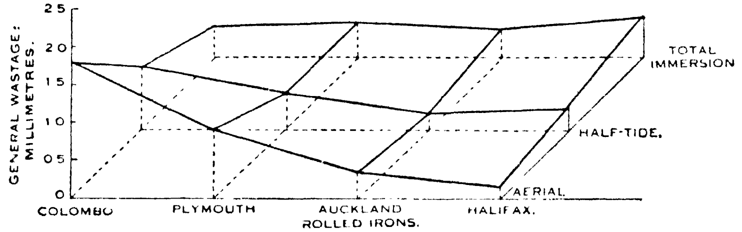


FIG. 1.

The surfaces of most industrially important metals exposed to the atmosphere become covered with a film, visible or invisible, which may influence subsequent corrosion processes. This film is frequently an oxide of the exposed metal, and its properties will vary with the metal and the conditions of exposure. It may largely protect the metal from further reaction, *e.g.* the oxide layer on aluminium which hinders the attack of many salt solutions, and the oxide layer on copper which appreciably slows down atmospheric attack. Of special interest is the resistance of the stainless alloy steels to the corrosive attack of many atmospheres and solutions ; this is probably largely due to the protective effect of complex oxide layers formed on their surfaces. On ordinary carbon steels, however, the oxidised layer has little or no protective capacity when the metal is freely exposed to attack by the atmosphere, or by salt solutions or industrial waters. The films formed by exposure to atmospheric conditions may be so thin as to be almost or quite invisible, but heating the metal surface increases the reaction rates and may produce thicker films which show interference colours. Still thicker films formed on steel, for instance, show inherent colours, and may crack and flake away locally during cooling and this may cause a localised electrochemical attack if the metal is exposed to the action of a salt solution. The thick film which remains on the metal acts as the cathode of an electrolytic cell with the bare metal as anode. Then, if there is an ample supply of oxygen to the cathode, and the ions in the electrolyte do not react to form an insoluble, impervious film at either electrode, localised action or pitting may occur at the anode.

Further discussion will now be grouped under two headings, dealing with atmospheric and immersed conditions respectively, to be followed by rather more specific treatment of corrosion in sea-water and in soils. In a survey of this kind it is impossible to give complete references to original work ; the references in the text must therefore be regarded only as general guides, and for bibliographical details and more extended information the reader is referred to the following works: "Metallic Corrosion, Passivity and Protection," by U. R. Evans; London, Edward Arnold & Co., 1937. "Corrosion, Causes and Prevention," by Frank N. Speller; New York, McGraw-Hill Book Co., 2nd ed., 1935. "Bibliography of Metallic Corrosion," by W. H. J. Vernon; London, Edward Arnold & Co., 1928.

Atmospheric Corrosion.

It has been mentioned that atmospheric corrosion comprises reactions of both the metal-gas and the metal-liquid type. By the latter is understood any reaction into which water enters, but not necessarily one in which the presence of liquid is evident to the eye. Investigations have shown that in air containing the usual traces of impurities it is not necessary for the meteorological dew-point to be reached for reactions of the second type to occur; the appropriate conditions are frequently realised well below saturation provided a critical humidity is exceeded, the precise value of which depends on the metal and on other factors. Atmospheric corrosion phenomena may be considered, therefore, as falling into three groups: (1) The relative humidity is consistently below the critical humidity. (2) The relative humidity, either continuously or periodically, rises above the critical humidity. (3) The metal is freely exposed to the open air, and is thus subject both to rain and to relative humidities that vary over the widest possible range. Conditions below the critical humidity favour, by direct oxidation, the formation of invisible oxide films, which may sometimes have an important bearing on the subsequent course of attack; usually, however, it is the *mode of breakdown* of the film that is of major importance and in this respect the common metals present varied but characteristic features. Both the formation and breakdown of primary (invisible) oxide films will therefore be considered.

FORMATION OF PRIMARY (INVISIBLE) OXIDE FILMS.—Most metals undergo oxidation on exposure to air or oxygen. The process may be regarded as reversible, *i.e.* $M+O \rightleftharpoons MO$, the direction depending upon the pressure of atmospheric oxygen. The minimum pressure required to send the reaction to the right is, however, for base metals excessively low at ordinary temperatures and for noble metals excessively high; this, in fact, constitutes a useful distinction between these classes of metals. It is now known that apparently clean surfaces of metals are frequently covered with invisible films of oxide and the properties of these thin films have within recent years been studied by gravimetric, optical, photo-electric, and electron-diffraction methods.

The invisible oxide film on copper confers marked protection against tarnishing (*infra*) provided that the thickness exeeds a critical value which appears to be such that the unit lattice of cuprous oxide is completed for the whole surface (Vernon, J.C.S. 1926, 2273). Rate of oxidation increases rapidly with temperature, the relationship being given by the equation $d \log W/dT = -Q/RT^2$, where W corresponds to corrosion rate (conveniently weight-increment after a given time) and T is the absolute temperature. This expression, which is identical in form with the empirical equation of Arrhenius, was developed independently by Dunn (Proc. Roy. Soc. 1926, **111A**, 203) from quantum principles for the special case of metallic oxidation. For copper, experimental agreement (linear relationship between log W and 1/T) has been established from 50° to 200° (Vernon, *ibid.*) and, without change of constants, from 250° to 600° (O. F. Hudson *et al.*, J. Inst. Metals, 1929, **42**, 243). The lower range includes the temperatures within which characteristic interference ("temper") colours are produced, first, second, and third orders of colours being discernible. The relationship between oxidation and time throughout both ranges of temperature is given consistently by a quadratic parabola, as would be expected on the view that thickening of the film proceeds by lattice diffusion of oxygen through an envelope the continuity of which is always maintained. The thinner films have been identified by Darbyshire (Trans. Faraday Soc. 1931, **27**, 675), using electron-diffraction methods, as consisting of cuprous oxide, Cu_2O; this has a lattice structure very similar to that of metallic copper, and there can be no doubt that the process is one of direct oxidation. At ordinary temperatures, in atmospheres of appreciably high relative humidity, the process appears to be more complex and it is probable that hydroxide enters into the composition of the film.

For aluminium and for lead, oxidation-time curves show an extremely protective type of film; exponential in form in the early stages, the curves rapidly flatten towards the time axis, with which they become nearly parallel in about 10 days, the estimated thickness of film then being about 10^{-6} cm. Preston and Bircumshaw (Phil. Mag. 1936, **22**, 654) have shown by electron diffraction that the oxide film on aluminium at room temperature is amorphous and that crystallisation does not commence until the temperature reaches 680°. Zinc is remarkable inasmuch as in ordinary air (free from local pollution but containing the usual traces of impurities) oxidation follows a linear relationship with time. The interpretation of this is not altogether clear, but is probably associated with the breakdown and repair of the primary film. The main film is granular in structure and does not show interference colours; access of atmosphere to the metal must be assumed to take place through relatively wide interstices in the film instead of by diffusion through a continuous envelope (Vernon, Trans. Faraday Soc. 1927, **23**, 159).

The formation of the invisible oxide film on iron presents a number of distinctive features. It was formerly thought that in the absence of factors that give rise to rusting the oxide film at ordinary temperatures ceases to thicken, whilst still extremely thin, almost immediately after formation. It has, however, been shown (Vernon, Trans. Faraday Soc. 1935, **31**, 1668) that growth of film proceeds continuously, although on ordinary massive metal interference colours do not develop unless the temperature rises above a critical value of very nearly 200°. Below this temperature the film takes on a brownish appearance which, beyond darkening, undergoes no further change on prolonged exposure. At higher temperatures the first brown or "straw" colour progresses continuously through the familiar sequence of "temper colours." Relationship of oxidation with temperature follows the equation

$$d \log W/dT = -Q/RT^2$$

above and below the critical temperature, at which there is a change of constants resulting in an increased slope of the log W–1/T curve at the higher temperatures. The oxidation-time curves are quadratic parabolas above 200°, but below this temperature they are modified considerably and correspond approximately with the empirical equation $W^{2\cdot5} = Kt$. Electron diffraction evidence has confirmed that these changes are associated with a change in the structure of the primary film, *i.e.* γFe_2O_3 below and αFe_2O_3 above 200° (Preston and Bircumshaw, *per* Vernon, *ibid.* 1677). *See also* H. R. Nelson, "The Primary Oxide Film on Iron," J. Chem. Physics, 1937, **5**, 252.

Some of the primary oxide films may be removed from the metal by suitable stripping processes. The oxide film produced on aluminium by heating in air was isolated (Seligman and Williams, J. Inst. Metals, 1920, **23**, 169) by dissolving away unoxidised metal in hot nitric acid, and that on ordinary unheated aluminium (Withey and Millar, J.S.C.I. 1926, **45**, 173T) by volatilising the metal as chloride in a stream of dry hydrogen chloride; a similar method was used (Sutton and Willstrop, J. Inst. Metals, 1927, **38**, 259) for isolating the film from anodically-oxidised aluminium. Evans (J.C.S. 1927, 1020, Evans and Stockdale, *ibid.*, 1929, 2651, isolated oxide films from iron and steel by the action of a saturated solution of iodine in 10% aqueous potassium iodide, or by anodic attack of the iron in a solution of sodium chloride; the films obtained were either fragmentary or complete according to the temperature and time of previous exposure.

Thin oxide films on iron have been studied spectrophotometrically by Constable (Proc. Roy. Soc. 1927, **115**, A, 570; 1928, **117**, 376), optically by Tronstad (Trans. Faraday Soc. 1934, **30**, 362) using a special technique (reported in a long series of papers) depending on the change in properties of a beam of polarised light after reflection at the metal surface, and electrometrically by Miley (Carnegie Schol. Mem., Iron and Steel Inst. 1936, **25**, 197) who measured the milli-coulombs of electricity required to reduce the film. Valuable contributions have been made by each of these methods, but the thickness of the film cannot yet be stated with certainty and this branch of the subject is in active development.

HIGH-TEMPERATURE OXIDATION.—The properties of oxide films or "scales" formed at temperatures higher than those hitherto considered become of importance in many industrial operations. Pilling and Bedworth (J. Inst. Metals, 1923, **29**, 529) found that the ordinary metals could be grouped in two divisions according to the relation between the densities of the metal and the corresponding oxide. Thus, if the oxide occupies a greater volume than the metal from which it is produced, then the film or scale is under a lateral compression which maintains it in a compact and hence protective condition (neglecting possible cracking which may occur under certain conditions), whereas if the oxide occupies a smaller volume its more attenuated condition deprives it of protective value. The first group is represented by most of the heavier metals, typically copper, iron and nickel, the second group by certain of the light metals, typically calcium and magnesium. A further corollary of the continuous nature of the film in the first group is the appearance of interference colours at appropriate thicknesses and also the quadratic relationship between film thickness and time. The latter follows because the rate of diffusion through the continuous envelope is inversely proportional to the thickness reached, *i.e.* $dW/dt = k_1/W$, or $W^2 = 2k_1t + K$, where W represents thickness of film in time *t*, and K is negligible over a wide range of temperature. On the other hand, films of the second group are characterised by absence of interference colours and by a linear relationship between film thickness and time, *i.e.* $W = k_2t$. Aluminium behaves anomalously for a light metal, because its oxide/metal density ratio places it in the first group and its oxide film is in fact extraordinarily protective. On the other hand, it neither exhibits interference colours nor is its oxidation/time curve a quadratic parabola; actually the deviation is in the direction of a cessation of oxidation, the explanation of which is still not altogether clear, although it is obviously associated with some special property of the alumina film. Preston and Bircumshaw (*l.c.*) showed that the vitreous film formed at lower temperatures crystallises slowly when heated at 680° to form γAl_2O_3. In the case of iron the constitution of the scale becomes more complex at higher temperatures. Pfeil (J. Iron and Steel Inst. 1929, **119**, 501) has identified three distinct layers, of which the outside layer is lowest and the innermost layer the highest in iron. Pfeil concludes that the oxidation of iron at these temperatures does not proceed by the simple "one-way" diffusion of oxygen through the scale to the metal, but by a "countercurrent diffusion" in which iron also passes outwards through the scale layer. Pfeil points out that this mechanism does not preclude a parabolic relationship between time and oxidation (Portevin, Prétet and Jolivet, *infra*, found the parabolic law to hold good for pure iron at 825°, 950°, and 1,000°), but it serves to explain a number of peculiarities in the scaling of iron and iron-rich alloys. The work of Wagner (Z. physikal. Chem. 1933, **39**, 328; 1934, **40**, 521) suggests that a similar mechanism may apply in the case of other oxide and tarnish films (*see also* L. E. Price, Chem. and Ind. 1937, **56**, 769, Hoar and Price, Trans. Faraday Soc., 1938, **34**, 867).

Relationship with temperature follows in general the equation already given for low temperature films (*supra*), *i.e.*

$$d \log W/dT = -Q/RT^2.$$

(In the case of iron the break in the log W−1/T curve at 200° may be conveniently regarded as dividing "low temperature" and "high temperature" oxidation.) The uniformity of this relationship is dependent upon the atmosphere remaining unpolluted. For example, minute traces of hydrochloric acid have an extraordinarily marked stimulative effect upon oxidation rate at all temperatures, the mechanism being probably catalytic in character (O. F. Hudson, Herbert, Ball and Bucknall, J. Inst. Metals, 1929, **42**, 221). Substances such as carbon dioxide and steam which are neutral at lower temperatures become actively oxidising towards iron and steel at high temperatures, whilst a small amount of sulphur dioxide may profoundly increase the rate of oxidation. The influence of furnace gases containing these substances has been investigated by J. W. Cobb and collaborators, W. H. Hatfield, C. Upthegrove, and other workers (*see* "Review of Oxidation and Scaling of Heated Solid Metals," H.M.S.O., London, 1935).

The problem of heat-treating iron and steel work in neutral atmospheres ("close annealing") with the object of avoiding subsequent "pickling" for the removal of scale, has received much attention industrially, and various suitable types of furnace are now available. The difficulty of this problem arises from the extremely low pressure of oxygen or other oxidising gases that is needed for oxidation to occur and the difficulty obviously increases considerably with rise of temperature.

Alloys for resisting oxidation at high temperatures most frequently have iron, nickel or (for the lower limits) copper as the basis metal with additions, most usually, of chromium or aluminium. These metals have a remarkable influence on the oxidation/time relationship, the normal parabolic curve being depressed towards the time axis. This effect, which becomes more marked with increasing alloy additions, has been shown for aluminium on brass by Dunn (J. Inst. Metals, 1931, **46**, 42), and for aluminium and chromium on iron by Portevin, Prétet and Jolivet (Rev. Met. 1934, **31**, 186). For further information on this subject the D.S.I.R. "Review of Oxidation and Scaling" (*supra*) should be consulted.

"TARNISHING," "FOGGING," RUSTING (BREAKDOWN OF PRIMARY OXIDE FILMS).—On exposure of metals at ordinary temperatures, under sheltered conditions, other phenomena besides the formation of oxide films usually intervene. The typical cases of copper (with zinc and brass), nickel and iron will be considered.

The characteristic feature of copper at low relative humidities is its susceptibility to tarnishing by extraordinarily minute traces of sulphur compounds, corresponding in their effects to hydrogen sulphide although their precise nature is uncertain. The reaction is typically of the metal-gas type; it is greatly facilitated by rise of temperature, and is hindered by the presence of thin films of moisture. The characteristic colours are generally believed to be due to the interference of light in a continuous transparent film. Although homogeneous physically, this is composed of a mixture of cuprous oxide and cuprous sulphide (extremely similar in lattice structure) with a large preponderance of cuprous oxide. The curve connecting thickness of tarnish film with time is essentially a quadratic parabola; when once started this develops with remarkable regularity and is quite unaffected by wide fluctuations in the degree of atmospheric pollution. In other words, the rate constant is dictated by properties of the initially formed film, which in turn depends on the conditions of atmospheric pollution which prevailed when the clean specimen was first exposed. An extreme case is presented when at the outset the air is pure or nearly pure—a condition that may be realised during summer months in the absence of local pollution. Exposure for a sufficient time then produces an invisible film of oxide which confers immunity from tarnishing on subsequent exposure to atmospheres containing the usual content of reactive sulphur. A similar effect is produced by preheating in air, when the minimum thickness required for protection (*supra*) is obtained by an hour's exposure at 75°. The film of oxide serves effectively to keep sulphur atoms out; on the other hand, a thin film of sulphide, by facilitating entry of both sulphur and oxygen atoms, increases the rate of subsequent tarnishing. The parabolic oxidation/time curve of copper, the continuous film of reaction product, and the characteristic interference colours are in marked contrast to the linear relationship given by zinc, the granular nature of the reaction product, and the absence of interference colours. The behaviour of brass is intermediate between that of copper and of zinc, the oxidation/time curve being compounded of the parabola and the straight line. The microstructure of tarnished 60–40 brass shows that the alpha (copper-rich) constituent behaves similarly to copper, giving a continuous tarnish film, whilst the beta (zinc-rich) constituent shows the discontinuous (granular) structure that characterises the film on zinc (Vernon, Trans. Faraday Soc. 1924, **19**, 886; 1927, **23**, 159).

The tarnishing of silver by sulphides is dependent on the presence of oxygen (Hahn, Z. anorg. Chem. 1917, **99**, 118). The loss of reflectivity of silver and silver alloys in indoor atmospheres is also greatly dependent on the surface condition (Vernon, 1924, *ibid.*). Reflectivity methods for following the tarnishing of copper, silver and nickel alloys have been developed by Kenworthy and Waldram (J. Inst. Metals, 1934, **55**, 247) and W. P. Digby (J. Roy. Meteorol. Soc., 1937, **63**, 163). The reaction, $3SO_2 \rightarrow S + 2SO_3$, which is stimulated by light (Konstantinova-Schlezinger, J. Phys. Chem. (U.S.S.R.), 1935, **6**, 601) may play a part in tarnishing processes, since silver and copper are known to be susceptible to attack by elemental sulphur at ordinary temperatures and the main sulphur-containing impurity in air is normally sulphur dioxide. Light also stimulates appreciably the "fogging" of nickel (*infra*).

In the processes so far considered, rate of attack is controlled mainly by properties of surface films. Nickel provides an example in which relative humidity becomes a controlling factor (Vernon, J. Inst. Metals, 1932, **48**, 121). In indoor atmospheres the polished surface frequently takes on a creamy-white film, a phenomenon conveniently described as "fogging." Here the mechanism is entirely different from that of tarnishing. First, the action depends on the presence of traces of sulphur dioxide as distinct from hydrogen sulphide (*supra*). But whereas the tarnishing effects of traces of hydrogen sulphide are displayed characteristically at low relative humidities, the corrosive effects of sulphur dioxide come effectively into operation only when the humidity exceeds a critical value in the neighbourhood of 70%. Thus, a polished surface of nickel either retains its brightness indefinitely or rapidly assumes a creamy film according as the relative humidity remains below or rises above the critical value. The initial mechanism most probably consists in the catalytic oxidation of atmospheric sulphur dioxide at the metal surface and the reaction of sulphur trioxide with water to give sulphuric acid. In the early stages the film contains free sulphuric acid and may be removed simply by wiping with a cloth; later it passes into a basic sulphate which cannot be removed without abrasion of the underlying metal. A similar process takes place with copper, but the magnitudes involved are of entirely different orders. With copper a definite concentration of sulphur dioxide has been recognised (approximately 0·9%), which must be exceeded for free sulphuric acid to appear; with nickel, this minimum concentration, although unknown, is excessively low and falls well within the amounts normally present in the atmosphere. Thus, under ordinary conditions, above the critical humidity, the influence of sulphur dioxide is very marked on nickel, but trifling on copper, whilst below the critical humidity the influence of hydrogen sulphide is marked on copper and (within ordinary atmospheric limits) negligible on nickel. Copper-nickel alloys, therefore, may show either one effect or the other, falling off in intensity either from the copper or the nickel end of the series, according to the relative humidity of the atmosphere.

The rusting of iron presents a number of points of contrast with each of the foregoing processes and constitutes a well-defined third type of attack. It is commonly stated that "iron does not rust above the dew-point," but this is erroneous for most conditions. For example, in an ordinary room atmosphere the relative humidity of which is kept at a low value by artificial means, an initially clean surface may undergo very considerable rusting. A distinguishing feature is that the attack commences at isolated, sporadically distributed centres; even at a relatively advanced stage the discontinuous nature of the rust can be detected with the aid of a lens. Two further points must be observed. (1) If, after the iron has been allowed to rust in the manner described, the relative humidity is increased to a high value (but still short of saturation) the rate of rusting increases enormously. (2) If the initially clean specimen is screened behind a single thickness of muslin (in form of a "cage") so as to intercept suspended particles, rusting does not occur and the original bright surface is maintained (Vernon, Trans. Faraday Soc. 1927, **23**, 159). It follows from (1) that critical humidity phenomena in the case of iron have a special significance, and from (2) that iron is extraordinarily susceptible to the influence of suspended (disperse) particles of solid or liquid matter in the atmosphere. The screened condition is favourable for the development of the primary invisible oxide film already discussed, and if a specimen has been so exposed for a sufficient length of time, it enjoys a certain degree of immunity from rusting on subsequent normal exposure. After a considerable time-lag as compared with a freshly-cleaned specimen, the primary film breaks down and rusting proceeds in the usual discontinuous manner.

The influence of both gaseous and solid pollution on the rusting of iron in relation to the relative humidity of the atmosphere has been studied (*ibid.* 1935, **31**, 1678) by experiments in which humidity was increased in steps from zero at the start to a maximum of 99%. The following conclusions are based on these experiments. A similar series of changes occurs either on initially clean specimens in atmospheres containing traces of sulphur dioxide, or on specimens initially "inoculated" with traces of various substances in an otherwise pure atmosphere. In either case primary and secondary critical humidities are exhibited (Fig. 2). The former, which occurs at 50 to 60% R.H., marks the point at which breakdown of the primary film occurs and attack on the metal commences. The surface becomes gradually covered with a very fine "rust," beginning at isolated centres, but even prolonged exposure fails to produce severe corrosion; the rust that is formed, however, is in a peculiar physical condition and is potentially extremely active. Thus, at the secondary critical humidity (approximately 80% R.H.) a relatively enormous increase in corrosion occurs, with the production of ordinary red rust. This greatly increased attack is due entirely to properties of the primary rust, for it proceeds just as rapidly if sulphur dioxide (when this is the initiating cause) is completely removed from the system just before the critical humidity is reached. The first critical point is associated with optimum atmospheric conditions for the commencement of rusting. The second point must be associated with certain physical properties of the initially formed rust; it is explained by Patterson and Hebbs (Trans. Faraday Soc. 1931, **27**, 277) on the basis of Zsigmondy's theory of gel structure. At the lower humidities water is held closely within the capillaries of the gel (the primary rust) and there is a state of mutual compression between rust and water; at the secondary critical humidity the capillaries are filled, the state of compression is released, and water is free to pass from the surface of the rust to the surface of the metal. As a matter of practical interest it may be observed that the phenomenal increase in attack at this point probably contributes materially to the removal of a protective coating, when, through porosity, rusting once occurs beneath it.

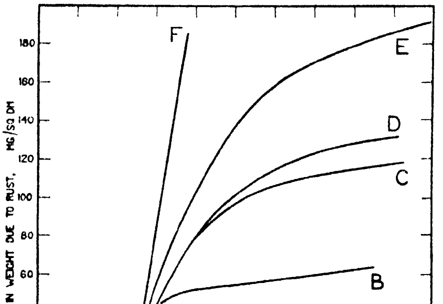


FIG. 2.

Curve.	Nature of particles (if any) on specimen. (Where present, uniformly 0·4 mg. per sq. dm.)	Nature of addition (if any) to atmosphere (purified air).
A	None or, charcoal or, quartz	None
B	Ammonium sulphate	None
C	None	0·01% Sulphur dioxide
D	Quartz	
E	Ammonium sulphate	
F	Charcoal	

Particles of solid matter which commonly enter into atmospheric pollution fall, from the corrosion standpoint, into three groups: (*a*) intrinsically active (dissociating mineral salts) such as ammonium sulphate in the neighbourhood of towns or sodium chloride near the sea; (*b*) intrinsically neutral but capable of adsorbing active gases from the atmosphere, *e.g.* various forms of amorphous carbon; (*c*) intrinsically neutral with negligible capacity for adsorption, such as crystalline silica. Only particles of the first two types are important in atmospheric corrosion. With the first, the combined presence of traces of sulphur dioxide in the atmosphere and particles at the metal surface produces effects at the secondary critical humidity that are almost exactly additive. When, however, the particles are capable of adsorbing sulphur dioxide and so increasing its local concentration at the metal surface, the effect is more than additive; for example, charcoal particles have a relatively enormous stimulative influence in the presence of traces of sulphur dioxide. Doubtless a similar effect is produced under service conditions by carbonaceous particles normally present in urban atmospheres. These several points are illustrated by the curves in Fig. 2.

The influence of carbon dioxide on the atmospheric corrosion of iron has in the past been regarded as of considerable importance. According to the old "acid theory," a trace of carbon dioxide permits unlimited attack for the reason that the first-formed product, assumed to be ferrous bicarbonate, hydrolyses to give ferric hydroxide, with liberation of carbon dioxide, whereby a further equivalent quantity of iron is attacked. Investigation (Trans. Faraday Soc. 1935, **31**, 1693; *see also* Proc. Chem. Eng. Group, S.C.I., 1937, **19**, 19) has, however, shown this view to be untenable. So far from stimulating the corrosion of iron, carbon dioxide, at concentrations in the neighbourhood of and also considerably higher than the normal atmospheric content, has a marked repressive effect at ordinary temperatures. This has been shown for a variety of conditions, both "supersaturated" and unsaturated, and including the case where traces of sulphur dioxide (by which the attack is initiated) remain in the system. The effect appears to be directed towards the suppression of the extraordinary change at the secondary critical humidity. For most conditions the corrosion actually observed must depend on the balance between carbon dioxide and sulphur dioxide in the atmosphere. The influence of carbon dioxide on the corrosion of *zinc*, particularly under "supersaturated" conditions, is in marked contrast. In the absence of sulphur dioxide the effect is repressive, as for iron, although not to such a marked degree; when, however, sulphur dioxide is already present the addition of carbon dioxide stimulates further corrosion.

OPEN-AIR CORROSION.—Many of the foregoing remarks apply equally to indoor and to open-air corrosion, except in so far as the latter is affected by rain. The influence of this factor is not necessarily adverse; it may even be favourable if it removes a corrosion product that is acid or hygroscopic in character, as with nickel, or if rain is able to assist in the development of a product having protective qualities, as with copper. On the other hand, the rate of attack may be increased by the breakdown or removal of an otherwise protective coating.

In this country rain invariably carries dissolved sulphates; sulphur dioxide in slight traces is also widely disseminated and may be regarded as a normal atmospheric constituent. (Both solid and gaseous pollution are maximal in winter and minimal in summer.) The primary constituent of atmospheric corrosion products is in consequence usually the normal metallic sulphate which, by hydrolysis, may yield either hydroxides or basic sulphates, or in some cases carbonates through contact with carbon dioxide. Near the seaboard, chlorides or basic chlorides may predominate unless a town is near. It is evident that the attack on the metal may involve either the removal of a soluble salt or the assimilation of an insoluble deposit. To denote such processes as these Friend has proposed the terms "erosion" and "surrosion" (Fr. *sur*, on). By erosion is usually understood the removal of a metal entirely by mechanical, as distinct from chemical, processes. Nevertheless, in atmospheric corrosion some distinction is useful because frequently the two processes take place simultaneously, and hence the ultimate change in weight of the specimen or structure is the resultant effect of the two. The endurance of a metal may thus depend on its ability to develop a covering, in inland atmospheres, of basic sulphate, or in marine atmospheres of basic chloride.

The green patina on copper, the corrosion product after exposure (in this country) of some 10 to 20 years, was formerly thought to consist of basic copper carbonate and was attributed to the action of carbon dioxide as present in unpolluted air. Analyses of typical patinas show that in inland districts the product consists essentially of basic copper sulphate, associated with a minor proportion of basic carbonate, the latter being highest in town and least (typically 2·75%) in country samples (Vernon and Whitby, J. Inst. Metals, 1929, **42**, 181 ; 1930, **44**, 389; Vernon, *ibid.* 1933, **52**, 93; J.C.S. 1934, 1853). Near the seaboard the sulphate ion in the patina is replaced by more or less chloride, but when urban and marine conditions coincide basic sulphate greatly predominates over basic chloride. In all cases the patina contains a certain amount of extraneous wind-borne material. Basic copper carbonate is thus accessory either to basic sulphate or basic chloride and is most probably formed by partial hydrolysis of the initially-formed characteristic salt in the presence of carbon dioxide. Copper is not converted to green basic carbonate, as usually supposed, merely by exposure to moist air containing carbon dioxide ; either the metal must be completely immersed in the aqueous solution or the attack must be initiated in some other way. Small amounts of organic carboxylic acids are particularly active in facilitating the formation of secondary basic carbonate and are probably largely responsible for the relatively high proportion of basic carbonate in urban samples. In districts sufficiently remote from both town and sea (a condition not realised in this country) the green patina does not appear.

The formulæ to be ascribed to the basic salts in the copper patina depend on the period of exposure, maximum basicity being reached only after about 70 years. In the case of basic sulphate and basic chloride 1 molecule of the normal salt is then associated with 3 molecules of copper hydroxide. The formulæ thus correspond with the co-ordination compounds, $[Cu\{(OH)_2Cu\}_3]SO_4$ and $[Cu\{(OH)_2Cu\}_3]Cl_2$ each of which is represented in nature by a mineral, brochantite and atacamite respectively. Associated basic carbonate has a limiting basicity of only 1 : 1, as in the mineral malachite, $CuCO_3{\cdot}Cu(OH)_2$. Younger products contain higher proportions of normal salt, considerable amounts of which (sulphate or chloride) are leached out in the early stages by the action of rain; it is this process which gives rise to the familiar disfiguration of stonework underlying copper or bronze structures. On the other hand, the green basic salt, long before its final basicity is reached, is insoluble in water, and affords protection to the metal. This accounts for the longevity of copper roofs and suchlike, of which there are many notable examples. There is, however, some evidence that an underlying thin film of cuprous oxide may play a part in the protection. Arsenic is a usual constituent of these old roofs, and this element has been found to reduce the corrosion of copper sheet in the comparatively early stages.

An important directional effect, associated with the influence of prevailing winds, should be noted. Many copper structures have the green patina developed more perfectly on the windward side, particularly if this is directed towards a distant town or towards the sea. A similar principle will obviously apply to other metals in which the corrosion product is not of the protective type, with less desirable effects.

The tendency to build up a protective, insoluble coating on exposure to the open air, very strong in the case of copper when once the early stages have been passed, is usually negligible for ordinary iron and steel. (This statement refers to conditions in this and other industrial countries; but cases are on record where solid and gaseous pollution have been sufficiently low to permit the formation of a protective coating in the course of long exposure.) Under sheltered conditions, depending largely on meteorological and pollution factors, the first-formed rust may actually accentuate subsequent corrosion. Under conditions, however, such that from the outset the air is almost continuously saturated with moisture, an approximately linear relationship with time is followed when once the specimen is covered with rust. Similarly, on prolonged exposure to the open air, the initial effect observed under less drastic conditions forms only a small part of the total corrosion, and again an approximately linear relationship between corrosion and time is followed, the total corrosion being roughly directly proportional to the total amount of pollution that reaches the specimen. The atmospheric conditions prevailing in the very early stages of exposure exert, however, a very great influence in determining the subsequent rate of attack. The importance of this factor in tarnishing has been mentioned. In open-air corrosion it was demonstrated by J. C. Hudson (Trans. Faraday Soc. 1929, **23**, 177, 475) for a series of non-ferrous metals which yielded the following mean relative values: summer, 100; autumn, 187; winter, 261; spring, 154. Similar seasonal effects for ferrous materials have been reported by Schramm and Taylerson in the United States (1934, *infra*), while Daeves in Germany (Naturwiss. 1935, **23**, 655) has observed marked differences in country and town atmospheres. G. Schikorr (Z. Elektrochem. 1936, **42**, 107) reported on two parallel series of field tests carried out in Berlin and in the Grunewald, 7 km. distant. Fresh specimens of iron were exposed month by month and rate of rusting correlated with meteorological data; hygrometric conditions were very similar, relative humidity in each case being maximal in winter and minimal in summer. In the purer atmospheres the fluctuations in relative humidity produced comparatively little effect on rusting, but in the city there was a marked degree of parallelism between the monthly corrosion values and the means of the monthly humidity readings. These results are in harmony with laboratory work which shows that increase of relative humidity, up to saturation, has either a negligible or a profound effect according as gaseous or solid pollution is absent or present.

The influence of climatic conditions has been investigated for marine atmospheres in long-period field tests of the Institution of Civil Engineers (specimens of various irons and steels exposed at Halifax, Auckland, Plymouth and Colombo) the results of which have been described by J. Newton Friend in a series of reports; the 10-year tests were the last to be described in detail (" Deterioration of Structures Exposed to Action of Sea-Water," XVth Rep., Inst. Civ. Eng. London, H.M.S.O., 1935) representing up to 15 years' exposure. They have been surveyed generally by Robert) Hadfield and S. A. Main (1936, *l.c.*). Climatic conditions are also in course of investigation in a comprehensive series of field tests established by the Corrosion Committee of the Iron and Steel Institute and the British Iron and Steel Federation, under the chairmanship of W. H. Hatfield. These tests, which are conducted at fourteen stations distributed in various parts of the world, have been described in detailed reports by J. C. Hudson (*e.g.* Vth Rep. Corr. Ctte., Iron and Steel Inst., 1938).

The accompanying data (Table I) are taken from a table given by Hudson (1937, *infra*).

TABLE I.

RATES OF CORROSION OF INGOT IRON AND ZINC.

Station.	Years' exposure.	Rate of corrosion (10^{-6} in. per year).		Ratio.
		Iron.	Zinc.	
Khartoum . . .	1	42	21	2·0
Khartoum . . .	5	18	8	2·3
Abisko, N. Sweden	1	172	26	6·6
Aro, Nigeria . .	1	449	53	8·5
Basrah, Iraq . .	1	459	38	12·1
Singapore . . .	1	610	44	13·9
Apapa, Nigeria. .	1	815	45	18·1
Redcar	5	1,590	(534)	(3·0)
Farnborough . .	5	1,840	89	20·7
Llanwrtyd Wells .	1	2,100	118	17·8
Calshot	1	2,450	133	18·4
South Africa . .	1	2,620	174	15·1
Motherwell . . .	1	3,300	185	17·8
Woolwich . . .	1	3,690	149	24·8
Woolwich . . .	5	2,690	164	16·4
Sheffield . . .	1	4,390	579	7·6
Sheffield University	1	5,040	300	16·8

In the Fifth Report (*supra*) Hudson states that the results so far obtained do not indicate a marked difference in the corrosion rates of mild steel and ingot iron. The addition of 0·2–0·5% copper reduces corrosion by about 30%, and the joint addition of approximately 0·5% of both copper and chromium by about 40 or 50%. The influence of alloying with larger amounts of chromium, etc., is discussed under " corrosion-resistant alloys " (p. 388). Structural and extraneous factors must be borne in mind, particularly with respect to the incidence of wind and rain; this aspect has been emphasised by Liddiard (Proc. Chem. Eng. Group Soc. Chem. Ind. 1937). Crevices, where water can be retained after the rest of the structure is dry, are particularly liable to become centres of corrosion, likewise any place which receives excessive impingement of rain falling from a relatively large catchment area. Contact with non-ferrous metals should generally be avoided on account of the danger of enhanced electrochemical attack, with rain-water as electrolyte.

Of other metals commonly exposed to the atmosphere, lead, which shares with copper a wide application for roofing purposes, also resembles copper in developing a protective coating (probably mainly of sulphate) in industrial atmospheres and so assuring itself of of extreme longevity. In comparison with copper, however, it suffers æsthetically owing to the absence of any pleasing patina. Contact with new wood (particularly oak), likewise contact with mortar or cement, should be avoided, or else severe corrosion either from organic acids from the wood, or alkali from the cement may result.

Zinc is also used successfully for roofing, but much more frequently (*e.g.* galvanised iron) as a protective covering for iron, over which it has great superiority under most conditions of atmospheric exposure (*supra*). An acid type of atmosphere is the least favourable.

Aluminium, unalloyed, is resistant to town atmospheres (a good example of its durability is afforded by the Eros statue in Piccadilly Circus, London), but the magnesium-aluminium alloy, containing from 2 to 6% magnesium, is advantageous, particularly with respect to the less rapid deterioration of the polished surface. Alloys of the duralumin type are liable to severe corrosion both in industrial and marine atmospheres, but this may be largely overcome by previous " anodic oxidation " whereby the thickness of the natural oxide film is substantially increased.

Magnesium is noteworthy inasmuch as carbon dioxide enters definitely into the corrosion reaction (Whitby, Trans. Faraday Soc. 1933, **29**, 844), for which there is a critical humidity, and carbonate normally predominates over sulphate in the (hydrated) product. Although this product has no protective qualities, the rate of corrosion, in the absence of alkali chlorides, is not so great as is commonly supposed. The foregoing metals and their alloys are also discussed under a later heading (p. 388).

Reference may be made to the following symposia on atmospheric corrosion in which many phases of the subject were discussed, *i.e.* in 1934 (Proc. Amer. Soc. Testing Materials) and in 1937 (Proc. Chem. Eng. Group, Soc. Chem. Ind.).

Corrosion in Immersed Conditions.

Although the corrosion of metals immersed in acids, salt solutions, or industrial waters frequently follows an electrochemical course and is proportional to current flow as shown by Evans and Hoar (Proc. Roy. Soc. 1932, **137**, A, 355), it is not necessarily so in all conditions. Patten (J. Physical Chem. 1903, **7**, 153) has shown that hydrogen chloride dissolved in dry chloroform attacks zinc vigorously in spite of the fact that the chloroform has an extremely low conductivity, and experiments have shown that the corrosion of steel in " conductivity " water and dilute salt solutions of specially high electrical resistance must necessarily be largely independent of current flow between attacked and unattacked areas. When the action is electrochemical a large number of factors may influence both the rate and distribution of corrosion. A particularly interesting question is: What are the factors which divide up the metal surface into areas that are anodic (relatively attacked) and cathodic (relatively protected)? Answers that have been given are (1) physical differences in the metal resulting from the mechanical preparation of the surface, (2) discontinuities or points of " weakness " in the air-formed film which overlies the metal, particularly emphasised by U. R. Evans, (3) the presence of different phases within the metal surface, (4) differences of concentration of oxygen, and of ions in solution close to the metal surface, (5) discontinuities such as crystal junctions. It seems probable that only slight differences are required initially to differentiate the metal surface sufficiently to start corrosion. Subsequently, the unequal distribution and the properties of the reaction products may be more important factors in deciding the distribution of anodic and cathodic zones, and this matter is discussed in more detail later. The nature of the corrosion products may also decide the rate of corrosion; in extreme cases this rate may be either reduced to zero by self-stifling at the anodes or allowed to proceed at the maximum rate determined by such other factors as speed of oxygen supply, the concentration of hydrogen ions, etc., detailed in Table II.

TABLE II.

FACTORS WHICH MAY INFLUENCE CORROSION RATES.

Metallic Factors.

1. The electrode potential, which is determined by the chemical and physical character of the exposed surface.
2. The hydrogen overpotential.[1]
3. The presence of different phases in the metal surface (especially in acids).

Environmental Factors.

1. The temperature.
2. Partial pressure of oxygen.
3. The rate of supply of oxygen.
4. The concentration of H ions.
5. The concentration of metal ions.
6. The concentration and specific nature of other ions present.
7. The electrical conductivity of the solution.
8. The chemical and physical nature and the distribution of corrosion products.
9. Relative movement of liquid and metal.

For a given sample of metal at atmospheric temperatures and pressures the most important factors in approximately stagnant acid solutions are usually the concentration of hydrogen ions, the hydrogen overpotential, the presence of impurities, and the nature of the corrosion product; in many nearly neutral solutions and industrial waters the rate of oxygen supply is also important, and may be so even in dilute acids. In both types of condition the initial corrosive action may commonly be regarded as the passage of metallic ions, at anodic areas, from the crystal lattice into the solution leaving electrons in excess ($Me \rightarrow Me^{\cdot\cdot}+2\epsilon$); simultaneously, an equivalent number of hydrogen ions associate with electrons and leave the solution at cathodic areas on the metal surface ($2H^{\cdot}+2\epsilon \rightarrow 2H$). The hydrogen atoms thus formed may either build up molecules and appear as gas ($2H^{\cdot} \rightarrow H_2$) or they may react with any oxygen or other equivalent oxidising agent present to form water.

$$2H^{\cdot}+2\epsilon+O \rightarrow H_2O$$

It will be evident that the depletion of the electrolyte of hydrogen ions will give rise to an excess of hydroxyl ions with consequent alkalinity in the neighbourhood of the cathode. Hoar (Proc. Roy. Soc. 1933, **142**, A, 628) prefers to regard the process as a reduction of oxygen at the cathode

$$O_2+2H_2O+4\epsilon \rightarrow 4OH'$$

but on either view the net result is obviously the same. In weak acids and many salt solutions both hydrogen evolution and oxygen absorption may occur together, gas evolution being predominant in the acids and water formation in salt solutions. These actions can proceed rapidly with relatively base metals such as zinc and iron, and slowly or not at all with semi-noble or noble metals such as copper and gold. Copper yields hydrogen gas only from boiling concentrated hydrochloric acid, but is corroded rapidly in many solutions in the presence of oxygen at ordinary temperatures with formation of water. Gold is attacked only by very powerful oxidising agents such as aqua regia, which evolves chlorine gas, or in the presence of oxygen by solutions in which it forms complex anions. The distinction between the " hydrogen evolution " and " oxygen absorption " types of reaction, notwithstanding many intermediate cases where the processes occur simultaneously, is of much significance and becomes especially important in the consideration of methods of protection.

It is thus useful to consider metals from the point of view of their position in the Electropotential Series, which is given in Table III. This shows the single electrode potential of each metal when in equilibrium with a solution of a normal concentration of its own ions (*i.e,* of normal ionic activity); the potential of hydrogen, as exhibited by an electrode of platinum black saturated with hydrogen at a pressure of one atmosphere, and plunged in a solution normal with respect to hydrogen ions, is used as the arbitrary zero point of a " hydrogen scale " in which the potentials of all other metals are arranged. Base metals, *i.e.* those below hydrogen in the table, are conventionally regarded as possessing a relatively negative potential, and noble metals a positive one. The base metals can displace hydrogen from many solutions containing its ions, but the noble metals can only do so in special circumstances, *e.g.* when the concentration of noble metal ions is kept extremely low in the solution by the formation of complex ions containing the metal. The influence of concentration on the single potential may thus be important, and is expressed for any given ionic concentration, C, by the formula:

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[1] This term is explained later, p. 376.

$$E=E_0+\frac{RT}{nF}\log_e C=E_0+\frac{0{\cdot}058}{n}\log_{10} C,$$

at N.T.P., where E_0 is the potential at normal ionic concentration, n is the valency of the ion involved, RT and F have their usual meaning, and E is the potential at concentration C.

TABLE III.

The Electro-potential Series of Metals.

Metal.	Ionic state.	Potential in volts (on hydrogen scale).
Gold	$Au^{\cdot\cdot\cdot}$	+1·36
Platinum . . .	$Pt^{\cdot\cdot\cdot\cdot}$ probably over	+0·86
Mercury . . .	$(Hg)_2^{\cdot\cdot}$	+0·80
Silver	$Ag^{\cdot}$	+·080
Copper . . .	$Cu^{\cdot\cdot}$	+0·34
Hydrogen . . .	$H^{\cdot}$ (arbitrary zero)	±0·00
Lead	$Pb^{\cdot\cdot}$	−0·12
Tin	$Sn^{\cdot\cdot}$	−0·14
Nickel . . .	$Ni^{\cdot\cdot}$	−0·23
Cadmium . . .	$Cd^{\cdot\cdot}$	−0·40
Iron	$Fe^{\cdot\cdot}$	−0·44
Chromium . .	$Cr^{\cdot\cdot}$	−0·56
Zinc	$Zn^{\cdot\cdot}$	−0·76
Aluminium . .	$Al^{\cdot\cdot\cdot}$	−1·33
Magnesium . .	$Mg^{\cdot\cdot}$	−1·55

(This table is a condensed form of Table XXIV in " Metallic Corrosion, Passivity, and Protection," by U. R. Evans. London, Edward Arnold & Co., 1937.)

The expression " hydrogen overpotential " which has already been used may now be explained. Hydrogen gas is freely evolved from a surface of platinum black whenever the potential is made appreciably more negative than 0·0 on the hydrogen scale; from the surface of other metals, however, a notably more negative potential is necessary before hydrogen is produced either in the gaseous or the dissolved state. The difference between this negative potential and the equilibrium potential is known as the overpotential of hydrogen at the surface concerned. It may be an important factor in determining the rate of corrosion in an acid; for instance, a metal with a high overpotential, such as zinc, will evolve hydrogen and corrode slowly or not at all if chemically pure; but if it contains impurities of low overpotential embedded in its surface it will corrode more quickly, since hydrogen will be evolved in a continuous stream from the surface of such impurities. These may consist of another metal, alloy, metallic compound, or some form of carbon. Metals which exhibit low overpotentials include platinum, gold, palladium and iron, while mercury, zinc, lead and tin show the opposite phenomenon; the precise effect of any given metal, however, depends partly upon its surface condition (smoothness, etc.).

The cause of overpotential has been the subject of much work and discussion, and seems to be connected with the sluggishness of one or both of the reactions:

Hydrogen ion + Electron → hydrogen (atom)

or 2 Hydrogen (atoms) → hydrogen (molecule).

Referring to Table III, it will be noticed that the more generally chemically reactive metals have high negative potentials and occur at the bottom of the table, whereas the chemically sluggish metals occur at the top. It might be deduced from this that the position of a metal in the potential series would give direct information about its " corrodibility " relative to other metals in the series. The deduction would not necessarily be true, because the rate at which a metal corrodes, *i.e.* its corrodibility, is partly determined by factors independent of the metal itself, such as composition and movement of the liquid in which it is placed, and the rate of oxygen supply; if, therefore, a metal be placed in a solution other than that in which the determination of its single electrode potential was made, both its position in the series and its rate of corrosion may be altered.

From what has been said above it will have become clear that corrosion rates are largely determined by polarisation at one or both electrodes. Polarisation at steel cathodes may be due to films deposited from certain salts in solution (*e.g.* the sulphates and nitrates of zinc and lead) which either shut off the supply of oxygen or other cathodic depolariser, or poison the catalytic activity of the metal surface for the oxidation of hydrogen to water (U. R. Evans, J.S.C.I. 1924, **43**, 321T; Thornhill and Evans, Fifth Corrosion Report to the Iron and Steel Institute, 1938, 381). Polarisation at anodes may be due to the formation of " insoluble " bodies in close contact with the metal surface or, perhaps, to a local high concentration of metal ions at that surface.

The solutions chosen for the potential measurements are those in which the metals are freely soluble and no secondary insoluble products are formed; in other solutions and in industrial waters these conditions may not hold, and if they do not no opinion can be gleaned from the table as to the relative corrosion rates of the metals. To take as concrete examples the three metals iron, magnesium and zinc, the following is the order of their corrosion rates in the liquids mentioned, in presence of oxygen:

Distilled water.	*N*/10 KCl.	Strong KOH.
Fe	Mg	Zn
Mg	Zn	Fe
Zn	Fe	Mg

The top metal in each column is the most rapidly corroded and it will be noticed that any one of the metals may occupy any position in the list according to the selection made of the corroding liquid. The general explanation is that the rate of corrosion depends largely on the properties of the corrosion products; thus, in distilled water the hydrated oxide formed affords less protection to iron than it does to magnesium or zinc, but in strong alkali the zinc oxide is dissolved and the metal is readily attacked, while the iron and magnesium oxides are almost insoluble and form films on the metal surface which are highly protective, at any rate for a considerable time. Iron may thus be said to become " passive " in strong alkali as well as in nitric acid and chromate and bichromate solutions of fairly high concentrations. The passivity in these solutions seems to be mainly due to the formation of films of ferric oxide on the surface of the metal; highly protective films are formed only when the precipitation of the metal as oxide occurs at the moment of its entrance into solution, and the essential condition for this is the presence of excess of the precipitating agent at the metal surface. Passivity has been specially studied by Evans and colleagues (J.C.S. 1927, 1020, and subsequent papers) and has been shown to occur with other metals and solutions, when the essential condition is fulfilled of the production of an insoluble product (which is not necessarily an oxide) immediately at the metal surface and in the necessary physical state. Some examples of passivity may be regarded as the result of direct chemical oxidiation, others as caused by complete anodic polarisation. In general, a metal will only remain passive as long as it is immersed in the passivifying solution; if removed to another liquid it will usually corrode because of a lowering of the concentration of the requisite precipitant at the metal surface.

The influence of temperature on corrosion in neutral aqueous solutions depends in general on whether the system is open or closed. In open systems, as shown by Heyn and Bauer (Mitt. Kgl. Mat. Prüf. 1910, **28**, 62) and by Friend (Iron and Steel Inst., Carn. Sch. Mem. 1922, **11**, 13), the rate of corrosion of iron increases to a maximum in the neighbourhood of 80°, beyond which the normal stimulative effect of temperature is more than offset by the retarding effect due to expulsion of oxygen. In closed systems, on the other hand, the rate of corrosion increases continuously with rise of temperature (Speller, " Corrosion, Causes and Prevention," 1926, 144). Nevertheless, if *entry* of oxygen is prevented, this initial rate must fall off rapidly owing to the using up of oxygen in the system. Thus, the total corrosion can only become serious if oxygen is replenished through any cause. Corrosion at higher temperatures, in strictly closed systems, when oxygen initially present has become exhausted, may still proceed *with liberation of hydrogen;* the rate at which this reaction occurs, however, is usually so very much lower (with iron and steel and neutral or nearly neutral waters) that it cannot give rise to serious corrosion, although the presence of hydrogen from this cause may frequently be recognised in heating systems.

The influence of light on corrosion, notwithstanding its theoretical interest, does not in general constitute an important factor in corrosion problems. Experimentally it is frequently difficult to separate the effect of light from that of temperature. General observations concerning the influence of light on the corrosion of iron in aqueous solutions have been made by Friend and others (Carnegie Schol. Mem., Iron and Steel Inst. 1922, **11**, 116). Reference has already been made (p.370) to the influence of light on tarnishing and fogging phenomena. Under immersed conditions the particular function of light appears to be the stimulation of electrochemical action. Vernon (J. Birm. Met. Soc. 1919, **7**, 549) found that the illuminated areas of brass in acid solutions became anodic. On the other hand, Bannister and Rigby (J. Inst. Metals, 1936, **58**, 227; J. Iron and Steel Inst. 1936, **133**, 293), in a systematic investigation employing dilute solutions of potassium chloride, found that for several metals the cathodic process was stimulated, the effect in this case being dependent on the presence of oxygen.

The influence of concentration of salt solutions is complex, but attention may be called to the fact that in the strongest solutions (concentrations exceeding, say, *N*/2) the rate of corrosion of mild steel (also zinc) falls off with increasing concentration, mainly owing to the lowered solubility of oxygen. Heyn and Bauer (1908) and Friend (*ibid.*) showed that in certain conditions there was a well-defined maximum or " critical " concentration, but the precise form of the corrosion rate/concentration curve may be affected by various other factors (Bengough, Lee and Wormwell, Proc. Roy. Soc. 1931, **134**, A, 323; Evans and Hoar, *ibid.* 1932, **137**, A, 343; Bengough and Wormwell, IIIrd Rep. of Corr. Ctte., Iron and Steel Inst. 1935, 148).

It will now be apparent that the rate at which a given metal can corrode in an approximately stagnant liquid depends partly on the composition of that liquid, and that this rate may vary between zero and some very high figure. Magnesium, for instance, is passive in strong caustic potash solution, but if placed in *N*/10 sodium chloride will corrode so rapidly that it is difficult to measure the rate accurately. Iron is also passive in the alkali, but will not corrode nearly so fast as magnesium in *N*/10 sodium chloride. Reasons for this are the much more negative potential of magnesium, associated with its comparatively low overpotential so that hydrogen can be freely evolved on the metal itself; this discharge of gas is so rapid that depolarisation due to oxidation of hydrogen by dissolved oxygen plays no appreciable part in the corrosion process. On iron, however, hydrogen gas is not so rapidly discharged, and the rate of corrosion is largely determined by the rate of depolarisation, and this will depend on the speed of access of oxygen to the effective cathodic areas on the metal surface. This speed is determined by the convection currents and diffusion rates in the particular experimental conditions studied, and if the *N*/10 sodium chloride be approximately stagnant it will be so slow that the corresponding corrosion rate will also be slow and far below that of magnesium in similar conditions. If the solution be stirred the rate of corrosion of the iron will increase with the speed of stirring, but the rate of corrosion will not reach that of magnesium at any experimental speed so far tested.

An objection to the foregoing argument might be raised that owing to the rapid evolution of gas from magnesium in *N*/10 sodium chloride the liquid can never be regarded as stagnant, and the comparison with iron is, therefore, imperfect. This raises the question of the effects of the motion of salt solutions on corrosion rates.

It is not easy to produce complete stagnancy in a solution since convection currents are set up by very small temperature changes and by evaporation, but with a minimum of motion corrosion rates may be low owing to two factors:

(1) Restriction of oxygen supply.

(2) Restriction of the supply of ions to form soluble anodic products.

Magnesium will not be affected by (1), since oxygen plays no part in the process; it might be affected by (2) if the supply of chloride ions became very low in the solution owing to the formation of insoluble basic chlorides of magnesium. The main corrosion product is, however, magnesium hydroxide, and usually corrosion proceeds rapidly. Iron resembles magnesium in not forming stable basic chlorides, but the rate of corrosion of zinc (in a comparatively limited volume of solution) slows down owing to the diminution of chloride ions and the increase of alkalinity in the solution (weak alkalis protect zinc, but very strong ones can attack it).

With increased motion of the liquid the rate of corrosion of iron in *N*/10 chloride solution also increases, at first rapidly, and then more slowly, and this increase is, no doubt, mainly due to the increased amount of oxygen made available for depolarisation. The effect, however, is not the same in all solutions; for instance, in some types of hard water the effect of slightly increased motion is to raise the rate of corrosion, but more rapid motion depresses it almost, or quite, to zero (Heyn and Bauer, 1910, *l.c.*; Friend, 1922, *l.c.*; Forrest, Roetheli, Brown, and Cox, Ind. Eng. Chem. 1931, **23**, 1010). The distribution of corrosion is also gradually changed in the direction of greater localisation before complete suppression is effected. This phenomenon seems to be due to the formation of protective films consisting mainly of hydrated ferric oxide at all the potentially anodic areas. (In the presence of ions, such as chloride, iron will tend to travel an appreciable distance from an anode before it is precipitated as hydrated oxide). Distilled water readily shows this peculiar form of passivity, which unfortunately resembles some of the other forms of passivity in the fact that it does not persist if the metal be removed from the passivifying conditions; nor is it necessarily permanent in time even in those conditions. The protective film may gradually thicken and break down, and intense local corrosion may then occur. In the absence of the passivity just described, the rate of corrosion in ordinary salt solutions will increase continuously with speed of movement because of the large supplies of oxygen available for depolarisation. Thus Speller and Kendall (Ind. Eng. Chem. 1923, **15**, 134), using iron tubes which had not been previously freed from rust, found that corrosion increased continuously with increase in the velocity of water flowing through them.

The effect of motion in the case of solutions in which corrosion is mainly associated with hydrogen evolution is different from that discussed above. The rate of corrosion is usually depressed as the speed increases, apparently because of the rapid removal of hydrogen bubbles which would otherwise form nuclei at which increases of gas formation could occur—in other words, gas is evolved more rapidly at an existing bubble than at a metal surface (Whitman, Russell, Welling, and Cochrane, Ind. Eng. Chem. 1923, **15**, 672). Nevertheless, the rates of corrosion in such liquids are still so high that the possible effects of increased depolarisation by the rapid supply of dissolved oxygen are negligible.

The effect on steel corrosion in alkali chlorides of oxygen pressures from one to twenty-five atmospheres has been studied by Lee (Trans. Faraday Soc. 1932, **28**, 707) and Bengough and Wormwell (IVth Report of the Corrosion Committee, Iron and Steel Inst. 1936, 213). The effect depends largely on the experimental technique used in raising the pressure of the oxygen. If it be raised to two to five atmospheres before immersion of the steel in sodium chloride solution (*N*/2 or *N*/10,000) or in a hard tap-water, very little corrosion occurs (less than 5 mg. in 10 days on a specimen with a surface area of 15 sq. cm.). If, however, the steel be first immersed in the liquid and the pressure raised subsequently the amount of corrosion in 10 days will be 120–170 mg. according to the solution used. If air at 10 atms. pressure be substituted for oxygen, *i.e.* a partial pressure of two atmospheres of oxygen, the amount of corrosion in *N*/2 $NaCl$ will be increased to about 36 mg. in 10 days with the first method of exposure, as compared with about 90 mg. in the second method. It is noteworthy that the amount of corrosion in air is less than in oxygen at equivalent partial pressure. The amount of hydrogen evolved when the second, or more usual, method of exposure is used is not greatly influenced by increase of oxygen pressure, and the corresponding amount of corrosion is negligibly small in sodium chloride solutions. The corrosion/time curves are straight lines which show increasing slopes with increased oxygen pressure up to about 20 atmospheres ; at higher pressures the corrosion rates increase but slowly, perhaps because the corrosion products become hardened and so tend to restrict the movement of oxygen and ions in solution.

It will have become evident from the above discussion that the effect of increased supplies of dissolved oxygen may be negligible, stimulative, or repressive, according to the conditions of experiment. The fact that a high supply may, in certain conditions, ennoble, render cathodic, and protect a sample of iron or steel has led to the development of the " Differential Aeration Principle of Corrosion." Early work in this field was due to J. Aston (Trans. Amer. Electrochem. Soc. 1916, **29**, 449), R. J. McKay (*ibid.* 1922, **41**, 201) and U. R. Evans (J. Inst. Metals, 1923, **30**, 239), the last-named having developed the subject in many subsequent papers. The principle states that a piece of metal tends to become anodic and attacked at places on its surface where the oxygen supply is least, and cathodic and protected where the oxygen supply is greatest. An example of the principle was considered to be the behaviour of zinc or steel half-immersed in, for instance, dilute sodium chloride solution. Since the oxygen supply will be most rapid to those parts of the metal surfaces which are nearest the liquid surface, these parts should be cathodic and protected, and those lower down anodic and attacked. Many experiments showed this prediction to be confirmed. It became clear, however, that the composition of the liquid affected the result; thus, if ammonium chloride were substituted for sodium chloride no protection was obtained near the water-line. Accordingly, the explanation was incorporated that the protection in the solution of the sodium salt is not due to oxygen *per se* but to alkali which is formed where oxygen unites with cathodic hydrogen to form water. The alkali protects the metal by causing precipitation of ferric hydroxide on the metal at the moment iron ions enter solution. Thus the mechanism, as emphasised by Bengough and Wormwell (Proc. Roy. Soc. 1933, A, **140**, 399), consists essentially in the preferential development of *protective films* at the most oxygenated areas of the metal.

It was next found that the protection thus afforded was not necessarily permanent and that both zinc and iron could become heavily attacked at, and near, the water-line even in solutions of alkali chloride after long periods of partial immersion; in fact, the attack might be so rapid as to overtake and surpass that which occurred at the less aerated parts of the metal. The explanation seems to be that the film which is first formed is not completely protective, but slowly thickens and finally breaks down owing to secular changes; when this has occurred corrosion is very rapid at the breaks, because of the high supply of oxygen which, *per se*, normally acts as an accelerator of corrosion in stagnant liquids exposed to the air at ordinary temperatures. An alternative explanation of this water-line attack which begins after long periods of partial immersion is that the supply of alkali to the water-line gradually falls owing to diminution of corrosion at more deeply immersed areas, which become covered with hardened and protective masses of corrosion product.

The differential aeration principle has been used to explain many examples of the localised corrosion of iron and steel, often with little justification. Deposits of rust, for instance, have been stated to be not only the results of corrosion but also the causes of local attack; deposits of foreign bodies, such as sand, have been supposed to act similarly; holes and crevices in metal, to which access of oxygen is restricted, are supposed to cause pitting. None of these ideas is correct generally, though each may be true in particular conditions. Differential aeration actually appears to be only one of the factors which can influence the distribution of corrosion over the surface of a metal in particular conditions, and is often not the most important (Bengough and Wormwell, J.S.C.I. 1937, **56**, 349). Others are:

1. Differences in the surface conditions of a metal, *e.g.* roughnesses and phase-types.
2. The chemical composition of the electrolyte, which may become inhomogeneous when corrosion occurs.
3. The geometry of the metal-electrolyte-gas system.
4. Gravitational streaming.
5. Interfacial tension effects.
6. Breakdown of protective films by " ageing " and other causes.
7. The presence of foreign bodies, discontinuous mill-scale, etc.

From what has already been said, it will have become clear that corrosion is a highly specific phenomenon both as regards metal and environment, and corrosion velocities and distribution are difficult to predict from first principles largely because of the varying physical properties of corrosion products. In a single experiment these properties may vary with time and may change, for instance, from being highly protective to completely non-protective. Hence the importance of a knowledge of long-period corrosion tests carried out in many types of defined conditions. A series of such tests has been carried out (Bengough and associates, 1926–1937) principally with zinc, iron, and carbon steels, and in stagnant conditions, but many more will be required before the subject can be considered to rest on a satisfactory quantitative basis.

Corrosion Fatigue.—Discussion so far has been confined to the behaviour of metal in an unstressed condition. If a sample of steel, for example, be stressed to a definite extent and then immersed, the corrosion rate in acids is usually increased but in salt solutions is not much altered. If, however, the stress is frequently reversed during the corrosion process a somewhat complicated process of destruction or alteration of the metal may be set up, the result of which is not necessarily identical with that which would be predicted from measurements of the results of corrosion and stress separately; it is usually much more serious. Conditions that have been particularly studied are alternate tension and compression, alternate bending and alternating torsion. If by any of these means the stresses are varied in a regular manner through a range in which zero stress is the middle point, then the greater the range the smaller the number of alterations of stress a metal can withstand before fracture. In the absence of any appreciable amount of corrosion, *i.e.* if the experiments are carried out in a vacuum or in a dry inert gas, a metal may be expected to withstand an infinite number of stress alterations provided the stress-range is below a definite limiting value, which is known as the "fatigue limit." Since the determination of this value is a very long and tedious process, another value, known as the "endurance limit" is often determined instead. This is merely a stress range which has not produced fracture in a stated number of stress-cycles, and, as Gough (J. Inst. Metals, 1932, **49**, 17) has pointed out, has no meaning unless this number is given. Gough and Sopwith (*ibid.* 93) have shown that if tests be carried out in presence of air and moisture the curves showing the relation between stress-range and number of cycles withstood (commonly called SN curves) lie wholly below those conducted in a vacuum or inert gas, particularly with copper, brass, and mild steel; evidently corrosion has played a part in the result and the joint destructive action is an example of "corrosion fatigue." Much more serious deterioration may occur if a liquid corrosive agent, such as salt solution or some type of tap-water, be present in addition to air. In such conditions it may be impossible to find any true "corrosion fatigue limit," because fracture of the metal may occur at extremely low stress-ranges, or even in absence of stress, *i.e.* by corrosion alone. The common practice is, therefore, to determine what is really an "endurance limit" at a stated number of cycles, but in much of the literature this is frequently called a "corrosion fatigue" limit.

Fracture owing to corrosion fatigue begins with the formation of surface cracks which are narrow fissures with sharply pointed ends, and their formation and progress has been studied in detail by Gough and associates in a whole series of papers in recent years. In aluminium, the cracks appear to start owing to preferential corrosion along the sites of previously formed slipbands; they are numerous and small, and are most thickly distributed "in the region of maximum resolved shear stress intensity; they are thus directly related to the crystalline structure of the specimen and to the applied stress system." In general, the cracks do not follow the boundaries between the crystal grains, and do not necessarily start from the bottom of large surface pits produced by corrosion. Nevertheless, stress-concentration at the point of notches, etc., plays a part in the propagation of cracks when they have once been started. In the opinion of Gough (*l.c.*) the vastly increased velocity of corrosion under corrosion fatigue conditions, as compared with stressless corrosion, is "due to the effect of the cyclic strains on the porosity and rupture of the (wholly or weakly) protective films that tend to form under corrosive conditions." These films are, in the writers' opinion, identical with the anodic films which are believed, on quite other grounds, to be commonly formed on steel, for instance, when corroding in salt solutions or industrial waters. These films limit the rate of stressless corrosion in presence of a particular rate of oxygen supply, but if they were to suffer frequent rupture the corrosion rate with that same oxygen supply might be greatly increased. In this connection it is interesting to note that Speller, McCorkle, and Mumma (Proc. Amer. Soc. Test. Mat. 1928, **28**, 159; 1929, **29**, 238) have shown that certain passivifying agents, such as chromates, are able to reduce liability to corrosion-fatigue, doubtless by repairing the anodic protective film as fast as it is fractured.

For steel parts operating in water, the prevention or amelioration of corrosion fatigue by various surface treatments (*e.g.* nitriding, coatings of zinc, cadmium, synthetic resins, etc.) or by additions to the water (*e.g.* sodium dichromate and various emulsifying oils) has been discussed by Buchholtz and Krekeler (Stahl u. Eisen, 1933, **53**, 671) and many others (*see* especially, Sopwith and Gough, J. Iron and Steel Inst. 1937, **135**, 315). In the case of aluminium alloys complete immunity from corrosion fatigue under salt spray conditions was reported by Gerard and Sutton (J. Inst. Metals, 1935, **56**, 29) from a synthetic resin varnish applied to an anodically oxidised surface of duralumin and stoved for 2 hours at 150° (*see also under* "Corrosion of Metals: Protective Measures"). A. J. Gould (Engineering, 1936, **141**, 495) has shown that the endurance of steel wire under corrosion fatigue may be considerably reduced by rise of temperature.

References.—General surveys of the subject of corrosion fatigue, with bibliographies, have been given by H. J. Gough (1932, *supra*) and by A. Thum and H. Ochs, "Korrosion und Dauerfestigkeit." Berlin, 1937, V.D.I. Verlag.

Season-Cracking.—A phenomenon allied to corrosion fatigue is that of "season-cracking." This is exhibited characteristically by fabricated articles of certain alloys, particularly high-zinc brasses and nickel brasses ("nickel silvers") following heavy working by rolling or drawing, or insufficient annealing; action may be long delayed but may result in the disruption of the article, sometimes whilst still in storage. As with corrosion fatigue, corrosion and stress are the two main factors, but the latter, being static rather than dynamic (a survival from the previous history of the specimen) must be distinguished from the alternating stresses of corrosion fatigue. The corrosive agents that promote season-cracking are usually highly specific—*e.g.* caustic alkalis and strong nitrate solutions for mild steel, and for brass traces of ammonia (sometimes other atmospheric impurities) or mercury; a 1% solution of mercurous nitrate, with 1% free nitric acid, is used as a reagent for rapidly detecting season-cracking proclivities in brass. In further distinction from corrosion fatigue, season-cracks follow an intercrystalline rather than a transcrystalline course, the internal stresses tending to draw the crystal grains apart, hence facilitating penetration of the corrosive agent; it has been suggested that a process of "age-hardening," whereby some constituent is rejected from solid solution at the grain boundaries, may play a contributory part. Season-cracking may be prevented by excluding the corroding medium by means of suitable coatings; much the sounder procedure, however, is to eliminate or to reduce to safe limits, by appropriate heat-treatment, the residual stresses within the material. Much of the work on season-cracking has been carried out by H. Moore and co-workers; present knowledge of the subject is surveyed by J. D. Jevons (Metal Industry, 1937, **50**, 431).

Corrosion by Sea-water.

Corrosion by sea-water is a matter of such great industrial importance that it has received much attention in recent years. The extensive investigations of the Sea-Action Committee of the Institution of Civil Engineers ("Field Tests on Ferrous Materials," by J. N. Friend) may be especially mentioned (*e.g.* XVth Report, *l.c.*, 1935). Early workers in this field believed that a solution of sodium chloride, the chief salt in sea-water, could be used for comparative tests instead of the natural water itself provided it was of equivalent (approximately half-normal) concentration. Bengough and Lee (J. Iron and Steel Inst. 1932, **123**, 285) carried out experiments with the two and found marked differences. In sea-water, the corrosion of mild steel is accompanied by a much larger proportion of hydrogen evolution, which, in stagnant conditions, might correspond to one-half the total corrosion, but in half-normal sodium chloride solution only to about 5%. An increase of oxygen supply raises the corrosion rate of mild steel in sea-water by a smaller amount than in the pure chloride solution, and this is due mainly to the fact that an increase of oxygen does not much alter the rate of hydrogen evolution. Corrosion/time curves for mild steel in stagnant sea-water fluctuate about a mean position and the mechanism of the corrosion is probably rather complicated. This is only to be expected, since sea-water contains, in addition to sodium chloride, chlorides and sulphates of magnesium and calcium, and traces of a large number of other salts and organic matter. Largely, no doubt, on account of the last-named, it has not been found possible to prepare from inorganic salts alone a solution which would reproduce the corrosive effects of sea-water on mild steel.

The presence of bacteria in sea-water may also assume importance in certain cases. In the presence of nitrogenous organic matter, micro-organisms of the ammonia-producing type have been associated (Grant, Bate, and Myers, 1921) with a localised attack on brass condenser tubes caused by the selective solution of copper by the action of ammonia. Such organisms have obviously a limited field of activity, since copper is the only one of the industrial metals that is sufficiently susceptible to attack by ammonia. A more general vulnerability is probably offered to the action of sulphate-reducing bacteria which are very widely distributed (*see* "Review of the Physiology and Biochemistry of the Sulphur Bacteria," by H. J. Bunker, Department of Scientific and Industrial Research, Chemistry Research Special Report, No. 3, 1936), but restriction is here brought about by the fact that they are active only under anærobic conditions. Particularly favourable conditions are afforded in deep-seated sea-muds, as, for example, the extensive deposits in the Atlantic Ocean off Walvis Bay, South Africa. Periodic eruptions liberate large amounts of hydrogen sulphide, which not only can be detected by smell at great distances but have been stated to accentuate the corrosion of metal structures on land. These deposits have been investigated by Copenhagen (Union of South Africa, Dept. Comm. and Ind., Fish and Marine Biol. Survey Div., Investigational Report No. 3, 1934), who also found the mud at the sea bottom of Capetown Docks to contain iron sulphide formed by the reaction of bacterially produced hydrogen sulphide with the excess of iron compounds present in the dock water. Corrosion associated with sulphate-reducing bacteria can be caused (1) indirectly by the action of liberated hydrogen sulphide in solution or otherwise, or (2) more directly by the presence of the metal structure *in situ* where anærobic reduction of the sulphates is taking place. In this case it is now believed that the metal itself may take an active part in the reduction process (*see* "Corrosion by Soils," *infra*). Examples of the first process are provided in harbours and docks, more particularly in certain waters. The presence of metals at the sea bottom must usually be due to such adventitious causes as wrecks, and interesting cases have been described where cast iron cannon, long submerged in this way, have been completely "graphitised."[1] Nevertheless, the possibility of a stimulation of this type of corrosion by the presence of sulphate-reducing organisms must be borne in mind under any conditions in which the supply of oxygen, locally or otherwise, is likely to become depleted.

The corrosion of marine condensers presents a number of problems that have been systematically investigated over a number of years (Reports to Corrosion Committee of Institute of Metals by G. D. Bengough and co-workers, J. Inst. Metals, 1911 onwards). Corrosion is greater in harbour waters than on the high seas and increases with temperature and with speed of working. Turbulence at the inlet end will produce rapid corrosion of brass tubes, particularly if much entangled air is present, giving rise to characteristic "impingement attack." Localised corrosion may also occur through the settling of various deposits in the tubes. The failure of brass tubes sometimes takes the form of so-called "dezincification"; this has been shown to consist of an attack on the brass as a whole, followed by redeposition of copper *in situ*, and to be favoured by retention of the corrosion products as a membranous layer in contact with the metal. (For ameliorative measures, *see* p. 389.) The present position of condenser tube corrosion has been surveyed by R. May (Inst. Marine Engineers, 1937, **49**, 171).

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[1] The "graphitisation" or "graphitic softening" of cast iron may take place under various conditions such as encourage electrochemical action between iron and graphite in the system. It consists in the leaching-out of the soluble iron-rich anodic product with consequent enrichment of the residue in graphite, which (together with smaller amounts of other insoluble constituents, carbides, silicides, etc.) remains behind as a skeleton or matrix, the interstices becoming filled with sufficient iron oxides and hydroxides (produced by corrosion) to cement the whole loosely together. The original shape of the object is retained, but the specific gravity is greatly reduced and the material is softened sufficiently to permit cutting with a knife.

CORROSION (AND PROTECTION) OF SHIPS' HULLS.—The corrosion of ships' hulls comprises by far the largest scale practical problem associated with sea-water attack and calls for special consideration. It will be convenient to deal here with methods of protection specific to this problem (methods of protection in general are discussed later, p. 385). Sea-water seems to be more corrosive than many types of fresh water towards mild steel. Thus, Montgomery and Lewis (Trans. Inst. Engineers and Shipbuilders in Scotland, 1932, **75**, 391) state that "vessels trading continuously in fresh water, as in the Great Lakes of North America, suffer practically no corrosion of hull structure." Nevertheless, sea-water is not necessarily more corrosive than a fresh water, for hard Teddington tap-water (temporary hardness 21, permanent hardness 6 parts per 100,000) is actually more corrosive towards mild steel in stagnant conditions. Movement, however, depresses the rate of corrosion of the hard water but increases that of the sea-water, so that with rapid movement the sea-water is the more corrosive.

Stainless steels of the type containing about 18% chromium and 8% nickel resist the action of sea-water better than plain carbon steels, but are still too costly to use for ship construction. Paints are therefore used to protect hull structures, and if care is taken to apply them properly and periodically, shell-plating, frames, and beams should last 20–25 years at least. Special parts of the ship, such as the scour area of ashes from an ejector or where a discharge of water flows more or less continuously, may require renewal in much shorter periods.

There appears, however, to be a consensus of opinion among British and Continental observers that the corrosion of both steel plates and of rivets in the structure of ships' hulls has assumed rather more serious dimensions during recent years. In the absence of definite evidence, changes in the quality of the metal cannot be held responsible for the increased corrosion of plates; but with respect to rivets, many people believe that the substitution of "rimming" steel for solid steel or wrought iron in modern practice has had a prejudicial influence. (The use of rimming steel for the manufacture of rivets for ships' hulls is now prohibited by the Committee of Lloyd's Register of Shipping and certain other authorities.) If anything, the rivets should be slightly less vulnerable than, or slightly cathodic to, the plates, since a more generally distributed corrosion on the plates is preferable to a localised attack on the rivets. The use of copper steel has been suggested; although the intrinsic superiority of this material is not so marked in sea-water as it is in industrial atmospheres a special advantage is claimed for its application to ships' rivets, because it is slightly cathodic to ordinary mild steel when the two materials are in contact.

Turning to ships' plates, there is considerable evidence of changes in treatment, as distinct from changes in composition, which may have an important bearing on corrosion. It has long been customary to expose the plates to the weather, after leaving the rolls, with the object of removing mill scale. Formerly a generous time, amounting perhaps to many months, was allotted to this process; in recent years, however, the tendency seems to have been to cut down this time and to use partially descaled steel in the ships' hulls. It has been suggested, moreover, that the scale formed in modern practice is more difficult to remove than that formed in the older conditions; this matter is now being investigated under the auspices of the Corrosion Committee of the Iron and Steel Industrial Research Council. Removal of scale by acid pickling has not hitherto been generally adopted (except in the Navy), but this is a quick and efficient method, particularly if an inhibitor be used to reduce attack on the metal. The premature failure of paint coatings applied to partially descaled steel is often due to the weakness at discontinuities in the scale and is aggravated by mechanical causes; when once corrosion has started, deterioration of the paint is facilitated partly by alkali produced by corrosion and partly by a process of undermining which may cause scale and paint to come away together.

Besides incomplete removal of scale, the time allowed in modern practice for painting and particularly repainting is often quite inadequate to ensure efficient protection. The dry-docking of a vessel at the end of a cruise for the purpose of repainting the hull normally occupies the period of a 12-hour tide. The operations which must be completed within this time include the removal of marine growths, the removal of old paint, the drying of the metallic surface, the application of the anticorrosive paint and the antifouling preparation, and, finally, the drying of the coating. So far as the last-named process is concerned, the Paint Industry has responded to requirements by evolving special quick-drying compositions. The older linseed-oil type of paints yields good results provided a sufficient period of drying is allowed, and combined with a red lead base it provides a priming coat that is satisfactory for general work. For ships' hulls, however, such paints have been largely replaced by compositions, typically damar resins in solvent naphtha, that dry owing to the evaporation of a solvent, as distinct from the complex oxidation process that constitutes the "drying" of linseed oil. In recent years preparations with a bituminous (asphalt) base have come largely into use; these have the advantage of being both quick-drying and insulating, and thus provide a suitable intermediary between the steel and the antifouling paint, which frequently stimulates rather than prevents the corrosion of contiguous metal. Recent practice in the United States appears to favour the use of coal-tar and rosin, both in anticorrosive and in antifouling compositions (Gardner and Hart, Amer. Paint and Varnish Manufacturers Assoc., Circ. No. 397, 1931); the following anticorrosive is now used in the U.S. Navy Department (values in pounds per 100 gallons of paint): zinc oxide 187, venetian red 93, silica 93, rosin 146, coal-tar naphtha 383, coal-tar 48, manganese linoleate 130, beeswax 3·3. For the painting of steel hulls for fresh-water service, Speller (Mech. Eng. 1935, **57**, 358) quotes good results from a mixed pigment (red lead 75%, lead chromate 12·5%, zinc chromate 12·5%) in a treated tung oil medium. J. L. Bedale (Proc. Chem. Eng. Group, S.C.I. 1935, **17**, 89) gives the following as an average analysis of paint for protection of hulls in British Naval practice: 25% solvent (naptha, paraffin or white spirit), 35% soluble medium (resins and drying oils), 40% insoluble solid (zinc or iron oxide, etc.).

Assuming a satisfactory paint composition the success of the operation largely depends on prevailing atmospheric conditions; a film of moisture on the metal, even of invisible dimensions, will effectively lower the adhesion of the paint, whilst the occlusion of salt particles beneath the coating adds considerably to the difficulty. (Painting with white lead in the steel mill while the metal is still hot has been found to be advantageous, *see* Fourth Report of the Corrosion Committee of the Iron and Steel Institute, 1936.) The factors that militate against the success of painting under ordinary dry-dock conditions are complex enough to deserve greater time and attention than is usually accorded them if a satisfactory degree of protection is to be ensured. In practice the question resolves itself into one of economics. It is possible to secure not merely an equal but a definitely greater protection from corrosion than that obtained in earlier years ; but this is possible only by increasing the time and care expended on painting and drying with consequent greater cost. Which course to adopt is for engineers to decide ; but it may be asked whether economy would not be better served by greater attention to protective measures, with consequent reduced wastage of metal and paint, of which latter enormous quantities are probably discharged into the sea soon after the ship leaves dry dock.

Fouling of Ships' Hulls.—The "fouling" of ships' hulls by the accumulation of marine growths is not necessarily related to corrosion, for the trouble is mainly associated with the serious reduction in speed for which such growths may be responsible, and any corrosion directly attributable to this cause is usually relatively unimportant.[1] Nevertheless, it is convenient to discuss fouling together with corrosion, for the treatment of the ships' hull must take into account both phenomena. The growths comprise several main groups of organisms, chiefly barnacles and molluscs (both of which are commonly referred to as "shell") and certain "sea grasses" (a term which seems to be applied indiscriminately both to hydrazoa and algæ); many different species have been recognised (*see* comprehensive review by J. P. Visscher, U.S. Dept. of Comm., Bur. Fisheries, Document No. 1031, 1927). As illustrating the importance of the problem, Visscher states that "after vessels have been at sea for 6 or 8 months they frequently accumulate growths from 2–3 in. in depth, and vessels with from 50 to 100 tons of fouling are seen quite frequently." Growths up to 1,000 tons in weight have been reported, but these no doubt represent cases where dry-docking has been neglected. According to Visscher, speeds in regular practice are reduced by amounts up to 50% and fuel consumption increased up to 40%. The trouble also affects flying-boats, which, in the tropics, have sometimes been prevented from rising from the water.

The treatment consists in applying *over the ordinary corrosion-resisting paint* a preparation that will be inimical to the attachment of marine organisms or, more particularly, their spores; such preparations are usually described as "paints," but frequently they contain substances that would promote corrosion if not insulated from contact with the underlying metal. On the other hand, the bituminous primary coat that is commonly applied to ships' hulls, whilst protecting the metal against corrosion, offers no resistance to the lodgment of marine organisms, certain kinds of which have been found to eat through the coating. Antifouling preparations in common use owe their value almost entirely to their poisonous content; when this is exhausted, antifouling properties cease. The problem is, therefore, to ensure that the toxic matter is released by the "paint" in sufficient concentration over a reasonably long period of time. It is one of peculiar difficulty, because widely different conditions must be met. For example, inoculation of the paint surface with the minute spores, which subsequently grow *in situ* to large dimensions, takes place almost entirely whilst the vessel is in port, motion being inimical to their attachment; if, however, the solubility of the paint is adjusted to afford adequate protection during this period it dissolves at an inordinate rate whilst the vessel is cruising, with the result that its toxicity is rapidly exhausted. In practice a compromise is attempted and wide variations in the effective life of the antifouling paint occur. Visscher (*l.c.*) states that "under optimum conditions vessels foul within 30 days of the time of dry-docking." Orton (Trans. Inst. Marine Engineers, 1931, **43**, 276) questions, however, whether this figure is capable of general application (*see also* H. W. Keenan, J. Oil Col. Chem. Assoc. 1933, **16**, 67). Light has been found to be inimical to the growth of many fouling organisms, particularly barnacles, which flourish most in "shaded" areas (Visscher, *l.c.*);

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[1] Hedley and McLean (J. Assoc. S. African Mech. Elect. Eng. 1936, **9**, 223) report, however, that stainless steel of "18/8" type undergoes severe attack at places of attachment of barnacles.

Wolfgang Neu (Internat. Rev. ges. Hydrobiol. u. Hydrogr. 1933, **28**, 228) states that green colours of wavelengths 500–558 $\mu\mu$ are strongly avoided by cyprid larvæ. The use of suitably coloured preparations is therefore being advocated, also aluminium pigment (*infra*) for the purpose of repelling growth-forming organisms.

The properties of an antifouling paint will clearly depend largely on the nature of the medium or "matrix," which should resist the erosive action of sea-water for at least as long as the toxicity of the paint is maintained; various varnishes, gums, and resins are used for the purpose. Special attention is usually given to the area exposed to alternate wetting and drying (in practice a belt about 3 feet in width) where mechanical conditions reach their greatest severity. The mixture applied to this part (the "boot-topping composition") should have maximum toughness and resistance, for which purpose synthetic resins have proved especially valuable in modern practice. With regard to the toxic constituents, compounds of mercury and of copper have so far proved the most effective, their joint presence, in a fine state of subdivision, being considered to be advantageous; pine oil is believed to add to the toxicity. M. Lopez (Quim. Ind. 1929, **68**, 222) states that copper resinate (a green powder soluble in paint media) is preferable to most substances hitherto used, and gives results much better than those of the earlier paints. According to Keenan (*l.c.*) there is some relationship between molecular weight, effective toxicity, and structure, the cyclic aromatic organo-metallic compounds being less stable than the open-chain compounds. Good results have been reported (Gardner and Hart, *l.c.*) for an antifouling preparation used by the U.S. Navy Department, which is as follows (lb. per 100 gallons of paint): zinc oxide 212, silica 82, magnesium silicate 83, cuprous oxide 112, mercuric oxide 45, balsam rosin 202, coal tar 133, pine oil 74. The presence of coal tar and of rosin is noteworthy. Opinions, however, are divided as to the effectiveness of coal tar in antifouling preparations and its use is not generally favoured in this country. J. L. Bedale (*l.c.*, p. 383) states that in modern British Naval practice the submerged part of the hull is given two or more coats of anticorrosive paint, followed by one coat of antifouling composition, the latter being applied immediately before the dock is flooded, owing to its deterioration when exposed to air (the boot-topping composition is applied in the same way); the antifouling composition contains solvents similar to those in the protective paint (*supra*) with additions of poisonous compounds of copper, lead, arsenic or mercury. The use of chlorinated rubber as a medium, with additions of copper, mercury, zinc, arsenic or selenium, alone or in combination, has been introduced (Smith, Porritt, and Dyer, B.P., 1935), aluminium powder being incorporated to give a light-coloured surface inimical to organisms.

Corrosion by Soils.

Although corrosion of metals embedded in soils is not in general so common as in the atmosphere or under water, it nevertheless presents problems of some magnitude industrially. The economic importance of the subject, as it affects, for example, water mains, electric cables (sheathings), and suchlike, is reflected in the large-scale organisations for its investigation, particularly in the United States and in Holland; recently a committee with similar objects has been set up in this country under the auspices of the Institution of Civil Engineers and further developments must be expected.

The complexity of the conditions is indicated by the large number of factors which may enter into the process, *e.g.* the content of oxygen, moisture, and soluble matter (solid, liquid, and gas), hydrogen ion concentration, electrical conductivity, particle size, drainage; bacterial processes are in many cases of importance, likewise the presence of "stray" currents from electric railways, etc., which may stimulate "electrolytic corrosion." Fortunately many of these factors are interdependent, so that conditions relatively unfavourable to corrosion are by no means uncommon. Moreover, unless electrically stimulated from outside, and with the further possible exception of corrosion associated with bacterial action, the rate of corrosion generally tends to fall off with time because of the "self-stifling" of the anodic process.

Burns and Salley (Ind. Eng. Chem. 1930, **22**, 293) found that the corrosion of lead in moist, inert sands increased (within certain limits) with increasing particle size, also with moisture content of the sand and with oxygen concentration of the overlying atmosphere. Bassett (J.S.C.I. 1931, **50**, 161) attributed diminished corrosive attack on steel specimens embedded (laboratory experiments) in salted soils to a restriction of oxygen diffusion. The conclusion might reasonably be drawn from such experiments that corrosion should become negligible when oxygen is completely or almost completely absent. Evidence is accumulating, however, that many examples of quite serious soil corrosion in service occur under anærobic conditions and are therefore unconnected with the supply of oxygen. It has frequently been noted that the tendency for corrosion to take the form of pitting increases with the acidity of the soil. It has also long been known that metal structures, particularly of cast iron, are frequently more prone to undergo corrosion when embedded in heavy clay soil than in porous sandy soil. This has usually been attributed merely to increased retention of water in the neighbourhood of the metal. Recent investigations, however, particularly by von Wolzogen Kühr and Van der Vlugt in Holland (1934) and independently by Thaysen and Bunker in this country (Chemical Research Laboratory of the Department of Scientific and Industrial Research), have led to the conclusion that such corrosion is in many cases attributable to the influence of sulphate-reducing bacteria. These are anærobic organisms of the vibrio type (H. J. Bunker, Vth Rep. Corr. Ctte., Iron and Steel Inst. 1938, 431) which very commonly find in clay the conditions (*i.e.* presence of sulphates and exclusion of oxygen, together with the presence of minute amounts of organic matter) requisite for their activity. The organisms have the peculiar faculty of reducing sulphates, normally with liberation of hydrogen sulphide; they are typically anærobic, and while access of air does not destroy them they become active only when air is excluded. Their influence on corrosion under such conditions arises from the fact that they enable dissolved sulphates to act as " hydrogen acceptors " ; an alternative mechanism is thus provided for cathodic depolarisation which is normally dependent upon the supply of oxygen. It is probable that the process is also assisted by a certain amount of anodic depolarisation because (for example) iron ions entering into solution at the anode meet with hydrogen sulphide produced at the cathode and are precipitated as insoluble iron sulphide at some distance from the anode surface. It can be shown that the theoretical amount of iron converted to sulphide in this way is equal to one-quarter of the total iron corroded in the process ; and in fact the presence of a certain amount of iron sulphide in the primary corrosion product is a characteristic feature of this type of anærobic corrosion. Cast iron is particularly liable under such conditions to undergo " graphitisation " (*cf.* deep-sea corrosion, *supra*) no doubt owing to the presence of graphite facilitating the expulsion of hydrogen. In practice the structures most commonly affected in this way are cast iron water mains, and here graphitisation proceeds from the outer surface (occasionally, also, from the inner, water, surface) leaving an irregular but approximately annular section of graphitised material.

Probably the most effective method of reducing the attack on iron and steel pipelines, as will be evident from what has gone before, is by attention to the method of laying. In clay soils the interposition of a layer of sand, gravel or ballast is frequently advantageous; cinders, however, should be avoided on account of the acidity that may arise from the oxidation of sulphurous impurities. Of the protective coatings applied to pipe-lines, bituminous materials, both coal-tar pitch and natural asphalt, are most commonly used and are frequently reinforced with felt or hessian. The extensive researches on soil corrosion carried out in the United States by Logan and coworkers (U.S. Bur. Stands.) have been surveyed by K. H. Logan in a number of papers (*e.g.* Trans. Electrochem. Soc. 1933, **64**, 118; Trans. Amer. Soc. Civ. Eng. 1936, **101**, 811; Bur. Stands. J. Research, 1936, **17**, 181 ; *see* " Corrosion and Protection of Pipelines in U.S.A.", *in* " The Science of Petroleum," London, Oxford University Press, 1938, p. 747). In the corrosion of pipe-lines importance is attached to the influence of concentration cells caused by local differences, both physical and chemical, in the character of the soil in contact with the pipe; this leads to localised attack, but various other contributory factors are recognised. (For methods of soil corrosion testing, *see* "Symposium on Corrosion Testing Procedures," Amer. Soc. Testing Materials, 1937, 95). Under soil conditions little difference has been observed in the corrosion rates of cast iron, wrought iron, and steel (including low-alloy steels). Similarly R. M. Burns reports (Bell System Tech. J. 1 36, **15**, 20) that high purity lead, lead hardened with 1% antimony, 3% tin, or 0·03% calcium, when used as cable sheathing, show approximately the same resistance to corrosion, environment being of far greater importance than variations in the composition of the metal. Copper and high-copper alloys, however, corrode less than most of the ferrous alloys, except in soils containing hydrogen sulphide. Of metal coatings applied to the protection of iron and steel in soil, zinc (hot-dipped) is most extensively used ; the rate of corrosion of galvanised iron is less than that of either steel or zinc alone and when the coating is perforated zinc gives a certain amount of cathodic protection to the underlying metal. Lead, on the other hand, has a greater tendency than zinc to develop pits, and when used as a coating tends to accentuate, if perforated, corrosion of the contiguous iron. (*See also* " Corrosion of Metals: Protective Measures," *e.g.* bituminous coatings, p. 395).

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CORROSION OF METALS : PROTECTIVE MEASURES. Methods of combating corrosion may be considered as falling into three groups according as the result is achieved by (1) the control of external factors, (2) the use of corrosion-resistant alloys, (3) the use of protective coatings.

(1) Control of External Factors.

Methods of protection depending on the control of external factors differ considerably in detail. Frequently they consist in the removal of some harmful constituent from or the addition of inhibitive material to the corrosive medium. It follows from what has gone before that corrosive atmospheres can be rendered inocuous either by filtering out solid pollution or by suitably absorbing gaseous pollution; but such measures can evidently be applied only in very special cases. A possible and obviously efficacious method of approach is to remove the pollution at source and much progress is being made in this direction. In the light of the principle of critical humidity, corrosion can frequently be avoided by adjusting the relative humidity of the atmosphere so that it is maintained consistently below the critical value. A knowledge of general principles is particularly important, since it is clear that the corrosion mechanism must be understood before the appropriate kind of " brake " can be devised.

In the case of immersed corrosion, it is again evident that methods involving treatment of the corroding medium cannot in general be applied on the large scale ; but on limited scales and more particularly in enclosed systems such methods are, in fact, of great importance. The procedure to be adopted will depend upon whether corrosion is mainly of the hydrogen evolution or oxygen absorption type. As discussed in the general article the hydrogen evolution type of corrosion is encouraged by low p_H. Certain acid types of natural water may have their aggressiveness removed by suitable adjustment of p_H, usually by addition of lime, which in effect displaces corrosion from the hydrogen evolution to the oxygen absorption range, the rate of attack being at the same time very greatly reduced (Whitman, Russell, and Altieri, Ind. Eng. Chem. 1924, **16**, 665).

In cases where corrosion is inevitably of the hydrogen evolution type, use may be made of overpotential. A familiar example is the amalgamating of zinc electrodes for the prevention of local attack by the acid electrolyte; here the normal process, which would result in the liberation of hydrogen from the zinc surface, is suppressed because of the high overpotential of hydrogen in respect to mercury. An interesting practical application occurs in the acid pickling of iron and steel articles for the removal of surface oxide (scale and rust). Attack of the acid upon the metal, as distinct from the oxide, involves the liberation of hydrogen; hence this part of the process can be suppressed by such additions as will increase the hydrogen overpotential. For this purpose organic inhibitors are used, of which a varied choice is available; heterocyclic nitrogenous substances (*e.g.* pyridine) being particularly efficacious. Mann, Lauer, and Hultin (Ind. Eng. Chem. 1936, **28**, 159) examined the inhibitive effect of aliphatic amines on the acid attack of iron and concluded that the amount of surface blanketed by any given molecule (hence the efficiency of the inhibitor) is dependent on the length of the hydrocarbon chains, the nitrogen atom being held responsible for the actual attachment to the metal. Many proprietary inhibitors used in pickling iron and steel are derived from by-products of industrial operations, especially coal-tar. W. Machu (Korrosion u. Metallsch. 1937, **13**, 20) in a comprehensive survey, suggests that the inhibiting action at the cathode is due to the formation of a film having high electrical resistance.

An application of the overpotential principle occurs in connection with magnesium-rich alloys, the corrosion of which invariably follows the hydrogen evolution type. One of the uses proposed for these alloys is the manufacture of fuel tanks for aircraft, but difficulties arise from the introduction of " leaded fuels " for anti-knock purposes. The lead is used in the form of lead tetra-ethyl, and ethylene dibromide is added for the purpose of removing the lead in the exhaust gases. In the presence of water a complicated series of reactions causes deposition of part of the lead on the surface of the alloy which then becomes attacked with liberation of hydrogen. The organic inhibitor process consists in mixing with the fuel a small quantity of a petrol-soluble substance that will suppress the evolution of hydrogen from the alloy surface, and for this purpose quinoline, to the extent of about 1%, has been found to be extremely effective ; attack is inhibited, whilst the anti-knock qualities of the fuel are unimpaired (D.S.I.R. Rep. Chem. Res. Board, 1934–7, London, H.M.S.O., 1938).

In the case of corrosion processes the rate of which is controlled by the amount of dissolved oxygen, as commonly obtains with waters and neutral solutions under many service conditions, corrosion may be reduced to negligible dimensions by the removal of oxygen from the system. For this purpose both chemical and mechanical methods are employed. The former consist usually in the passage of water (which for economical working must be heated) over a large surface of iron, special precautions being taken to prevent the choking of the system by the rust produced. Suitable plant is described by Speller (" Corrosion, Causes and Prevention," 2nd ed., 1935). Other chemicals, such as sodium sulphite, are sometimes used for the removal of oxygen, but considerable care is necessary to avoid excess and the content of dissolved salt is in any case increased. There are many types of mechanical deaerators, from open heaters, in which a current of steam sweeps over the surface of the heated water, to heaters of the Elliott type, in which water is introduced into a chamber at reduced pressure, the sudden boiling on superheating serving to expel dissolved gases. For the deaeration of water in the cold a fine spray is injected into a chamber under high vacuum. Mechanical deaeration has the advantage of removing carbon dioxide and other dissolved gases besides oxygen, but complete elimination of the latter is probably best achieved by means of a supplementary chemical treatment.

Further methods of water treatment include the addition of substances that will (1) suppress the anodic as distinct from the cathodic process which is the function of the " inhibitors " previously considered, (2) lead to the formation of a film or scale over the whole surface. The first group comprises alkali additions (sodium hydroxide, sodium carbonate, or calcium hydroxide); these become less effective with increase in concentration of dissolved salts, particularly chlorides. It also includes chromates, which are frequently added to brine solutions for corrosion prevention. In either case such additions must be made with caution, for if, as is most often the case, the rate of corrosion is under cathodic control, *incomplete* suppression of the anodic process may result in its localisation, with consequent pitting. (This point has been emphasised by Evans (Trans. Electrochem. Soc. 1936, **69**, 213).) Sodium silicate has been used for the treatment of water intended to pass through iron and steel systems, but its success appears to be dependent on the presence of calcium and magnesium salts, which assist in the deposition of a protective coating. In the case of a saline water it must be regarded in the same category as the alkalis (*supra*) and appropriate care exercised in its addition. Nevertheless, on lead, in various types of water, silicate additions of the order of about 10 parts per million of sodium silicate, do undoubtedly produce strongly protective coatings; this confirms very early observations (Crookes, Odling, and Tidy, 1886), that water is " lead-proof " when it contains dissolved silica.

Organic colloids such as gelatine, agar, etc., also exert considerable protective influence in neutral solutions (Friend and Vallance, J.C.S. 1921, **121**, 466), the mechanism consisting presumably in adsorption of the disperse phase on the metal surface (such emulsoids are known to retard solvent action of various kinds when adsorbed at the solid/liquid interface). The comparatively long life of metal cooking utensils (particularly of aluminium) has been attributed to the colloids present in food. Patterson and Culbert (J.S.C.I. 1935, **54**, 327T) have described another type of inhibitor, represented by the restraining effect of polyhydric alcohols on the corrosion of iron in potassium sulphate solutions. Adsorption of the organic substance on the corrosion product was believed to be responsible for subsequent retardation, which was found to depend upon the number of hydroxyl groups per molecule of inhibitor.

Hard waters are in general less corrosive than soft waters because of their ability to deposit surface films that are protective in character. Provided carbon dioxide is not present in excess, incipient corrosion will often favour the precipitation of films by reason of cathodically produced alkali. In one successful method of water treatment for pipe-lines, just sufficient alkali is added to give a protective layer over the interior of the pipe. Very soft waters are sometimes treated with limestone in order to introduce film-forming constituents. The principles underlying the artificial treatment of natural waters for the controlled precipitation of suitable protective coatings have been developed mainly by Tillmans in Germany (*e.g.* Gesund. Ing. 1912, **35**, 669; Gas u. Wasserfach. 1931, **74**, 1097 *seq.*) and by Baylis in America (*e.g.* J. Amer. Waterworks Assoc. 1935, **27**, 220). In each case the primary object was the protection of the inner surfaces of supply pipes and the conditions sought were such as would produce a layer of calcium carbonate, or a mixture of calcium carbonate with rust. Tillmans' work was based mainly on the conception of the aggressive action toward calcium carbonate of waters containing more than a certain amount of free carbon dioxide; *i.e.* part of this carbon dioxide is required to keep bicarbonate in solution, hence it is only excess above this amount that enables water to attack calcium carbonate, so preventing the formation of a protective layer on the iron. The excess was called by Tillmans " aggressive carbon dioxide," a term which, it should be observed, refers only to aggressiveness towards deposits of calcium carbonate and not towards metal, although that may follow indirectly. (The direct action on iron, at ordinary temperatures, of such concentrations of carbon dioxide that are likely to be present in natural waters is very much smaller than was previously supposed and is probably negligible in most instances, although it may become significant at higher temperatures as in closed heating systems.) Aggressive carbon dioxide may be removed by contact with marble or limestone. Baylis (*l.c.*) has described examples of the successful application of these principles and has given curves connecting the determined p_H of the water with equilibrium values for alkalinity in terms of calcium carbonate. If for any given water the determined p_H falls above this curve, calcium carbonate will tend to precipitate out from the water and form a coating, whilst if below the curve the water is " aggressive " and tends to dissolve calcium carbonate. Baylis emphasises that the curve is modified by other constituents, magnesium carbonate, etc., and it is necessary to determine the calcium carbonate equilibrium point for each particular water by direct experiment. Lime is usually used to treat the water but soda can be used if it is desired to avoid an increase in hardness.

Problems connected with " external factors " under soil conditions are discussed in the general article (p. 384).

In power plants and in many industrial operations it is often necessary to use water from which scale-forming constituents have been removed in a softening process. Generally the need is dictated by objections arising from accumulations of deposits; in boilers, however, the presence of magnesium salts is deleterious from the corrosion point of view and their removal therefore becomes important. For reasons already considered, however, the softened water should be rendered slightly alkaline; small amounts of certain other materials are also commonly added for the purpose of producing protective films. Care is needed in using waters that have been softened by base-exchange processes because of their higher content of dissolved sodium salts; contact of dissimilar metals, *e.g.* steel with copper or brass, should be especially avoided. A method of ameliorating the corrosivity of such waters is to by-pass a certain amount of the raw water so that the treated water may have the necessary minimum degrees of hardness.

Corrosion in *refrigerating systems*, which affords good examples of protection by control of external factors, has formed the subject of a general discussion (Proc. Brit. Assoc. Refrigeration, 1936–7, **33**, 35). Corrosion may affect either the ammonia (refrigerant) circuit or the calcium chloride (brine) circuit, but appreciably so only in the presence of water in the refrigerant or of oxygen in the brine. A third possible contingency is the leakage of refrigerant to the brine; this must be especially avoided because of the formation of ammonium chloride, by which the hydrogen evolution (as distinct from oxygen-absorption) type of attack is actively promoted.

Electrochemical Methods of Control.—Corrosion in aqueous solutions and natural waters being an electrochemical process (attack on the metal proceeding from anodic points or areas) " electrochemical " or " electrolytic " methods aim at countering the natural process by rendering the whole metal surface cathodic, for which purpose an external electromotive force is employed. The principle is attractive and its application can be readily demonstrated by small scale experiments. Difficulties arise, however, on the large scale owing to the impossibility of distributing the current uniformly over the whole of a large area. For example, in condenser systems (in which electrolytic methods, at one time extensively tried, have been largely discontinued) anodes were inserted in the water boxes at the ends of the tubes, which themselves constituted the cathodes; in practice, however, no more than the first few inches of the tubes could hope to receive protection (Bengough and May, J. Inst. Metals, 1924, **32**, 245). Nevertheless, for the protection of pipe-lines in soil, where the function of an electrolytic method is to supplement the protection afforded by the usual protective coating, successful application has been claimed. Examples are quoted by K. H. Logan (*l.c.* " Science of Petroleum," 1938).

A method similar in principle to that of an externally-applied E.M.F. is the use of protector blocks, as, for example, the zinc slabs attached to bronze propellor blades and to the adjacent steel hull for the purpose of deflecting electrochemical attack from the steel structure to the readily-replaceable zinc. The method is limited by the (normally) very short distance to which the cathodic protection can extend, to meet which objection a series of such slabs are usually fitted. Much greater effective distances for the protection of duralumin by zinc were found by Akimov (Korrosion u. Metallsch. 1930, **6**, 84) and zinc plates are in fact used for the protection of the duralumin portions of wing-tip floats of aircraft (W. H. Hatfield, J. Roy. Aeron. Soc. 1935, **39**, 564). In closed systems zinc may operate by using up available oxygen; for example, Bannister and Kerr (Trans. Liverpool Eng. Soc. 1933, **54**, 15) reported equally good protection from zinc blocks attached to steel boiler plates when electrical contact was prevented, showing that in this case protection was chemical rather than electrochemical.

(2) Corrosion Resistant Alloys.

It was formerly considered that increase in the corrosion resistance of a metal could be effected only by more complete purification or by additions such as would render it more " noble " or intrinsically more resistant. Much more commonly in modern practice the result is achieved by additions that are themselves intrinsically more reactive, the rapidly formed initial film imposing increased resistance to subsequent attack. Much depends on environment, and an alloy that will develop a highly resistant film under one set of conditions may fail to do so when the conditions are changed, a fact that must be borne in mind in the selection of materials for various purposes.

Iron-rich Alloys (*Stainless Steels, etc.*).—Industrial non-rusting steels fall into two main groups: (1) Chromium steels, represented typically by ordinary " stainless steel " containing 13–14% chromium; these are capable of being hardened by quenching from a suitable temperature. (2) Austenitic nickel-chromium steels containing typically 18% chromium, 8% nickel; these alloys cannot be hardened by quenching. A third type, more recently introduced, contains 16–20% chromium and about 2% nickel. As this is non-austenitic it resembles the first group in its ability to harden, whilst in corrosion-resisting properties it is intermediate between groups (1) and (2). The typical alloy of the first group is similar in chromium content to Brearley's original material (1913), but carbon now ranges from 0·1% (the so-called " stainless irons ") to about 0·3% as in stainless cutlery, and methods of heat-treatment have been improved. There is considerable evidence that the stainless properties conferred by chromium are due to the presence of a tenacious oxide film, rich in chromium, that is self-healing, provided that environmental conditions are sufficiently oxidising, and provided also that the surface is smooth—preferably " bright-polished." Ordinary stainless steel is highly resistant to tap-water, fruit juices, and all oxidising acids (contact with strong nitric acid actually strengthens the passive film and improves subsequent resistance), but is readily attacked by non-oxidising acids (*e.g.* hydrochloric and sulphuric), by which the passive film is destroyed. Particles of chlorides as in marine atmospheres and of soot in industrial atmospheres are inimical, and the surface should therefore be wiped frequently under such conditions. In sea-water its resistance is only moderate and it is liable to anodic attack when in contact with non-ferrous materials.

The presence of nickel in the " 18–8 " austenitic alloy, coupled with the fact that the added elements are in solid solution, gives a greater range of stability to the invisible passive film, and in particular a greatly improved resistance to sea-water with freedom from electrolytic corrosion in contact with ordinary steels and non-ferrous materials. The alloy has also an improved resistance to sulphuric acid and, although to a much less extent, hydrochloric acid; further resistance is obtained by the addition of molybdenum (typically 2·5%) and certain other elements. Austenitic stainless steels are especially resistant to oxidation at high temperatures, but if they are maintained for any length of time at temperatures between 500° and 900° (as in welding) they are liable subsequently to an intercrystalline type of corrosion (" weld decay ") due to the partial rejection of chromium carbide to the grain boundaries. The condition can be removed by appropriate heat-treatment or, alternatively, may be prevented by the addition of small amounts of certain elements (*e.g.* titanium) which have the effect of retaining carbides in solution; niobium (about 10 times carbon content) being less easily oxidised than titanium) is recommended for steels that have to withstand the most drastic welding treatment. Heat-resisting steels have been surveyed, with extensive bibliography, by W. H. Hatfield, J. Inst. Fuel, 1938, **11**, 245.

For large-scale structural work, for which stainless steels would be too costly, copper steels, containing 0·25 to 0·5% Cu, are available. The increased resistance to corrosion (which has been identified with the formation of a copper-rich surface film) is more particularly observed in industrial atmospheres high in sulphur dioxide. Rusting is not prevented, but it is less destructive in character. Moreover, such steels provide an improved bond both for paint coatings and for galvanising. Chromium-copper mild steels, containing approximately 1% chromium, 0·5% copper, are stated to show improved corrosion-resisting properties over ordinary copper steels (*see* p. 374).

High silicon cast irons containing from 13 to 15% silicon (" duriron," " tantiron," etc.) are much used in chemical engineering for acid pumps, etc. Their resistance to sulphuric and nitric acids is very high. A similar alloy (" durichlor ") containing the same amount of silicon with 3·5% molybdenum is stated to be especially resistant to hydrochloric acid, its relative immunity being very probably due to the formation of an insoluble coating of molybdenum chloride. (For handling hydrochloric acid in chemical engineering practice it is, however, generally advisable not to depend upon resistant alloys but to use where possible either glass-lined or rubber-lined equipment.) Austenitic cast irons, containing typically 14% nickel, 6% copper, 2% chromium, have, besides greatly improved mechanical properties, a high resistance to many kinds of chemical attack, comparable with and sometimes superior to that of phosphor bronze (J. G. Pearce, Proc. Chem. Eng. Gp., S.C.I. 1934, **16**, 91; A. B. Everest, *ibid.* 1937, **19**, 69). They have also high resistance to oxidation by heat, with freedom from " growth," to which ordinary cast irons are liable after repeated reheatings.

Nickel-rich Alloys.—The high resistance exhibited by nickel towards many industrial liquids, particularly alkalis, is shared markedly by its principal alloys. Of these, monel metal (a " natural " alloy of nickel and copper smelted direct from the mixed ore) is the most typical and most widely used. It contains approximately 68% nickel, 28% copper, 2% iron, remainder manganese, silicon, etc. Similar alloys are prepared synthetically. They are characterised by generally good resistance to non-oxidising acids, *e.g.* monel metal is widely used for pickling equipment using hot dilute sulphuric acid. It is also very suitable for superheated steam fittings, pumps, etc. Monel metal has only a fair resistance to hydrochloric acid (although better than either nickel or copper alone); greater resistance is obtained by the substitution of molybdenum for copper, and this is the basis of certain proprietary alloys recommended for use with hydrochloric acid. All the " non-oxidising acids " have their corrosivity greatly increased by aeration. This is shown by the following figures, due to Thompson and McKay (Ind. Eng. Chem. 1923, **15**, 1114) (for specimens moving at 15 ft. per min. immersed in dilute sulphuric acid at 82°C.):

	Corrosion Rate. Mg. per sq. dm. per day.	
	Air-free (washed with methane).	Air-saturated.
Copper .	43	1,070
Monel metal	64	700

The advantage of an " air-healing " film as in 18/8 chromium-nickel steel is shown by the further data (Searle and Worthington) quoted by Moore and Liddiard (Chem. and Ind. 1935, **54**, 787).

	Loss of wgt., mg. sq. dm. per day, in 3% sulphuric acid:	
	Oxygen-free.	With oxygen bubbled through.
Monel metal .	17	630
18/8 CrNi steel	442	4

Alloys of nickel with chromium (*see also* in General article under High-temperature Oxidation) are used in dairy and other food industries and in chemical engineering, where high corrosion-resistance is required. " Inconel " contains approximately 80% nickel, 14% chromium, 6% iron. Nickel-rich (chromium-free) alloys are not good for oxidising acids (*e.g.* nitric acid); they have, however, extremely high resistance (not appreciably reduced by aeration) towards alkaline solutions, caustic soda and caustic potash. Aqueous ammonia is resisted if dilute, but stronger solutions are aggressive, particularly towards nickel-copper alloys. (For such conditions ordinary iron or steel, which is completely passivated by ammonia, may be used). Nickel alloys have a very high resistance towards sea-water (*see* " copper-rich alloys "). They are sensitive to attack by sulphurous acid solutions and by humid atmospheres containing traces of sulphur dioxide.

Copper-Rich Alloys.—Copper-rich alloys fall into two main groups, (1) copper-zinc alloys or brasses, (2) alloys of copper with other metals—principally with tin (the true bronzes), with aluminium (aluminium bronze), and with nickel (cupro-nickel). Of these the corrosion-resistance of the first group is generally less than that of copper, whilst members of the second group are in this respect at least equal to and frequently superior to copper. Whilst the brasses, therefore, are generally selected primarily for economic or mechanical considerations, additions being made where necessary for increasing resistance to corrosion, the resistance of the other alloys is frequently of major importance and, together with their superior mechanical properties, dictate their application in chemical engineering.

Brass is used extensively as tubes, etc., *e.g.* in evaporators and in condensers. Under certain conditions, particularly where insoluble corrosion product can accumulate in contact with the metal, as, for example, in marine condenser tubes, so-called " dezincification " may occur. The net result is a removal of zinc and enrichment of copper, but the process has been shown to consist in attack on the alloy as a whole followed by *redeposition* of copper, with consequent weakening of the material. Dezincification is more prone to occur in 60/40 brass which contains crystals of α and β solid solutions (the β zinc-rich constituent undergoing preferential attack) than in 70/30 brass which consists entirely of the α phase. The addition of 1% tin as in the Admiralty (70–29–1) alloy confers rather greater resistance, whilst complete immunity from dezincification is obtained under many conditions by the addition of 0·01% arsenic. Another type of rapid attack caused by the impingement of an aerated stream of water (" impingement attack ") has been overcome by the addition of 2% of aluminium, and this material (containing 76% copper, 22% zinc) is now widely used for condenser tubes; with the further addition of 0·02% arsenic for the suppression of dezincification, it has largely superseded Admiralty brass for condenser tubes. (For further information on marine condenser tubes, *see* references on pp. 381, 382.)

The copper-tin alloys find extensive application for pumps, valves, etc. and, with the addition of a little zinc (*e.g.* Admiralty gunmetal, 88 copper, 10 tin, 2 zinc), for various marine and other fittings. Phosphor bronze is a copper-tin alloy to which a small amount of phosphorus, up to 0·5%, has been added as a deoxidiser. They have good general corrosion resisting properties. The aluminium bronzes (copper with 5 to 10% Al), owing to the formation of a surface film of aluminium oxide, are useful in many conditions, as, for example, in contact with hot and cold sulphuric acid in moderate strengths; the alumina film also enables them to resist oxidation at high temperatures. The copper-rich nickel alloys strongly resemble the corresponding nickel-rich alloys in resistance to sea-water corrosion, particularly impingement attack (*supra*), and cupro-nickel tubes, approximately 70% copper, 30% nickel, are also widely used in marine condensers.

All the copper-rich alloys are vulnerable to nitric acid. Their response to non-oxidising acids depends in general upon whether or not the solution is aerated. In the absence of air, high resistance is shown, but severe attack may occur if air is admitted (*cf.* behaviour of copper, Thompson and McKay, *supra*). Resistance to caustic alkali solutions is good, but not so good as that of the nickel-rich alloys. The copper-rich alloys resemble copper in susceptibility to attack by aqueous ammonia and their use should therefore be avoided in the presence of this reagent. The use of copper alloys in chemical engineering has been surveyed by S. Baker (Proc. Chem. Eng. Gp. S.C.I., 1937, **19**, 41).

Aluminium and Magnesium Alloys.—Whilst the use of aluminium and magnesium alloys is most commonly dictated by considerations of lightness and "strength-weight ratio," their resistance to corrosion may assume great importance, as, for example, in aircraft exposed to sea-spray. Aluminium differs from the metals previously discussed in that its highest corrosion resistance is characteristically exhibited in the unalloyed state; this is because of the continuity of the thin covering film of oxide to which the metal owes its normally good corrosion resistance, notwithstanding its intrinsically reactive character. Recent developments in the industrial electrolytic refinement of aluminium have led to a product of highest purity (exceeding 99·99%) from which extraordinarily high resistance to chemical attack by acids and by sea-water has been reported (R. Gadeau, Chem. et Ind. 1935, **34**, 1021). Certain of the aluminium alloys having maximum strength, duralumin, etc. (*see* previous volume under "Aluminium") contain such alloying elements as copper and zinc which reduce the efficiency of the natural protective film; such alloys are best treated by the anodic oxidation process or by a "metal-cladding process" (*see under* "Protection by Coatings," *infra*). Magnesium and silicon, however, have a much less injurious effect on the natural film and certain alloys containing these elements are much used for atmospheric and sea-air conditions; examples are "Mg7" and "Hydronalium" (approximately 7% magnesium). The addition of small amounts of antimony as in the German "K.S. Seewasser" alloy is claimed actually to increase (by formation of antimony oxychloride) the resistance of the natural film to sea-water. In alloys of the duralumin type the presence of copper confers valuable age-hardening properties, but such alloys, if the necessary heat-treatment has been imperfectly conducted, are liable to undergo intercrystalline corrosion, particularly in marine atmospheres. Aluminium and its alloys are used over a wide range of conditions, structural, architectural, industrial, and domestic. For cooking utensils they have the advantage of complete non-toxity. Owing to the solubility of aluminium in alkalies, alkaline conditions should in general be avoided; for the cleaning of aluminium utensils ordinary soda should be replaced by preparations containing sodium silicate which is much less harmful.

The greater lightness and favourable strength-weight ratios of magnesium-base alloys (*e.g.* "elektron" types ranging from 90 to 96% magnesium, with additions mainly of aluminium, manganese, and zinc) have encouraged their use within recent years. The readiness, however, with which magnesium oxidises superficially is not offset, as with aluminium, by the resistance of the oxide film towards marine atmospheres; moreover, attempts to produce a protective type of oxide film by anodic processes, as for aluminium, have so far proved unsuccessful. Other protective coatings are available (*see* "Protection by Coatings," *infra*) that will resist severe salt-spray conditions, but at present there is considerable reluctance to displace the usual aluminium alloys for aircraft, although in other directions the use of magnesium alloys appears to be extending. Magnesium and magnesium-base alloys have extraordinary resistance to hydrofluoric acid (through formation of an insoluble film of magnesium fluoride) and also (in contrast with aluminium) to alkalis and alkaline solutions. Other data are given by L. Whitby (Ind. Chem. 1931, **10**, 203). Alloys of the light metals have been surveyed by C. H. Desch (Proc. Chem. Eng. Group, S.C.I. 1937, **19**, 79).

Lead Alloys.—The corrosion-resistance of lead, which under many conditions is the main criterion determining its use, is associated, in contradistinction to aluminium, with a relatively low "intrinsic" reactivity; like aluminium, however, the freshly-cleaned metal becomes rapidly covered with a film of oxide which has marked protective properties (Vernon, Trans. Faraday Soc. 1927, **23**, 156). In contact with sulphuric acid this film is converted to relatively insoluble lead sulphate which protects the underlying metal from further attack, hence the great value of lead in the sulphuric acid industry. For this purpose high purity is essential, since most additions would impair the continuity of the film; a recent B.S.I. specification for "Type A chemical lead" requires not more than 0·01% total impurity. The addition, however, of 0·05% tellurium (advantageous for mechanical reasons) is stated to increase greatly the resistance of lead, and also of lead-antimony alloys, to sulphuric acid (Singleton and Jones, J. Inst. Metals, 1933, **51**, 71). Type B "hard lead" alloys contain usually from 10 to 15% antimony; they are much used in chemical plant, particularly for acid pumps. Alloyed with 10 to 25% tin, lead is used as a covering for iron ("terne plate") for roofing purposes (*see* p. 374). For cable sheathing, water-pipes, etc., lead is usually strengthened by certain additions, *e.g.* small amounts of antimony or tin, or traces of calcium; high-strength ternary alloys, containing cadmium (0·25%) with either tin (1·5%) or antimony (0·5%), and characterised by freedom from intercrystalline failure to which pure lead is liable under conditions of vibration, have been developed in this country (S. J. Nightingale, Dev. Rept. D.3, Brit. Non-ferrous Met. Res. Assoc. 1931). None of these additions, however, appears to affect appreciably the corrosion-resistance under soil conditions (*see* "Corrosion by Soils," p. 384) A similar conclusion probably holds good for most water conditions also; *see*, for example, Nightingale, *ibid.*; F. Mayer, "Wiener Hochquellwasser und Bleirohre," Berlin, 1934. Nevertheless, the susceptibility of lead to corrosion in soils containing decaying organic matter, and the "plumbo-solvency" of lead in certain natural waters must be borne in mind. The behaviour of lead and lead-base alloys towards natural waters has been surveyed, with extensive bibliography, by H. Ingleson (D.S.I.R. Water Poll. Res. Tech. Paper No. 4, London, H.M.S.O., 1934). Reference has already been made (p. 374) to the need for avoiding contact with oak; it is also desirable to insulate lead (*e.g.* by bitumen-impregnated felt) from contact with cement, which, in presence of moisture, may cause serious corrosion (D.S.I.R. Building Res. Bull. No. 6 (3rd ed.), London, H.M.S.O., 1935).

Tin Alloys.—For economic and other reasons tin is most widely used in the form of coatings on iron and copper, tinplate as used in the canning industry being the outstanding representative; familiar exceptions are tinfoil for the wrapping of foodstuffs, block tin for condensers (distilled water) and for the handling of beer, sheet tin for collapsible tubes (dental pastes, etc.). The principle tin-rich alloys are Britannia metal and pewter; formerly Britannia metal contained from 5 to 8% antimony, and pewter from 8 to 15% lead. Modern pewter, however, contains typically 5% antimony, 1 to 3% copper, and no lead. From the corrosion-resisting stand-point T. P. Hoar (J. Inst. Metals, 1934, **55**, 135) has shown that the presence of 5% antimony is desirable, but suggests that the further addition of 1 to 3% copper is deleterious.

Silver Alloys.—The application of silver and silver-rich alloys in chemical engineering is naturally limited by economic considerations, but a number of practical uses, particularly for resistance to attack by alkalis, both fused and in solution, has been described by D. McDonald (Proc. Chem. Eng. Group, S.C.I. 1931, **13**, 50). "Sterling silver" (92·5% silver, 7·5% copper) widely used for silver plate and ornamental work, is prone to discolour by tarnishing through the action of traces of sulphur compounds in the atmosphere. Reflectivity measurements (Vernon, Trans. Faraday Soc. 1924, **19**, 882) showed a reduced amount of tarnishing on sterling silver containing 1·75% cadmium, provided that the surface was brightly polished. H. A. Sloman (J. Inst. Metals, 1934, **54**, 161) found that the addition of as little as 0·5% beryllium to silver-copper alloys approximating in composition to sterling silver conferred a marked degree of immunity to tarnishing under quite drastic conditions, owing to the formation of a protective self-healing film of beryllia.

Zinc Alloys.—Although alloys in which zinc is the main constituent have little application as corrosion-resisting alloys there are cases in which corrosion becomes an important factor in determining their use. An example is that of the zinc-base die-casting alloys (approximately 4% aluminium) which, unless special attention is given to the purity of the materials, are subject to a form of intercrystalline corrosion, particularly under warm, humid conditions. The action is accompanied by a dimensional change or "growth" (for discussion, *see* Russell, Goodrich, and Cross, J. Inst. Metals, 1928, **40**, 239); this growth is probably caused by oxidation of zinc at the grain boundaries, hence the high oxide/metal volume ratio of zinc (p. 369) would be expected to contribute to mechanical failure. Minute traces of impurity (particularly lead) are primarily responsible and no trouble whatever is experienced when zinc of the highest purity (exceeding 99·99%) is employed. For zinc used as a protective covering to iron under urban atmospheric conditions the presence of lead is advantageous (W. S. Patterson, J.S.C.I. 1927, **46**, 392) no doubt owing to the accumulation of relatively insoluble lead sulphate in the product.

References (Books dealing with Corrosion-resistant Alloys): J. H. G. Monypenny, "Stainless Iron and Steel," 2nd ed., 1931, Chapman and Hall, London; McKay and Worthington, "Corrosion Resistance of Metals and Alloys," 1936, Reinhold Publishing Corporation, New York. *See also* works recommended under CORROSION, GENERAL (p. 368). Moore and Liddiard, "Corrosion-resisting Non-ferrous Alloys," J.S.C.I. 1935, **54**, 786.

(3) Protection by Coatings.

Protective coatings may be classified according as they have or have not a chemical bond with the underlying metal. The former include both "natural" and artificially stimulated coatings of oxide and certain corrosion products. The latter comprise chiefly (*a*) paints, varnishes, and such-like, (*b*) metal coatings.

Natural Protective Coatings.—A number of commonly used metals have appreciable resistance to corrosion by virtue of a film of oxide with which they are normally covered. Aluminium, for example, has a heat of oxidation among the highest of the common metals and yet is comparatively stable under many conditions. The formation of invisible oxide films on iron and copper has already been discussed; the "stainlessness" of stainless steel is due to the presence of a tenacious oxide film that is self-healing under slightly oxidising conditions. Such invisible protective films may not inappropriately be called "natural varnishes." A feature common to them all is that the protection breaks down, sometimes spectacularly, if the external conditions alter in such a way that the oxide film cannot be maintained.

A good example of a "natural paint" is provided by the green patina on copper. This is a genuine corrosion product and is characteristic of attack by air charged either with salt spray at the seaboard or with traces of combustion products inland, the essential constituent being basic copper chloride or basic copper sulphate, the latter, however, being much the more widely distributed (*see under* General article). The protective character of the patina is probably due largely to the continuity and insolubility of these basic compounds, although there is some evidence that a thin film of cuprous oxide, which is invariably found beneath the green deposit in immediate contact with the metal, plays an important part. Unfortunately, it is the exception for a natural corrosion product to behave in this way; frequently its presence encourages further attack on the underlying metal.

Artificial Coatings Reinforcing or Simulating Natural Protective Coatings.—Protective coatings of oxide may be produced by thermal, chemical, or electrochemical treatment. An old-established example of the thermal method is that of the Bower-Barff process for iron and steel, with its various modifications (Gesner, Bontempi, etc.) the essential part of which consists of heating the metal with superheated steam. Copper and copper-rich alloys may be protected against tarnishing by thin films of oxide produced by low-temperature heating in air (Vernon, J.C.S. 1926, 2273); these may either retain essentially the original appearance of the metal or, according to temperature and time of heating, give pleasing interference colours that are highly permanent as distinct from films of sulphide of similar initial appearance. Immersion in an oxidising liquid is sometimes employed, as, for example, the "chromate" dip for magnesium and the M.B.V. (Modified Bauer-Vogel) process for aluminium; but such coatings have the disadvantage that they are necessarily very thin.

The industrial importance of aluminium and its alloys led to various attempts to increase the thickness of the natural oxide film by electrochemical means. The first process for the anodic oxidation of aluminium was patented in 1924 by Bengough and Stuart, under the Department of Scientific and Industrial Research. In this process the metal is made the anode in a 3% solution of chromic acid at about 40°C., using a neutral cathode, usually of stainless steel; it is largely used for the protection of duralumin in aeronautical work (Sutton and Sidery, J. Inst. Metals, 1927, **28**, 24). Recent developments have been described by R. W. Buzzard (J. Res. Nat. Bur. Stand. 1937, **18**, 251). The process can be applied to other aluminium alloys containing not more than 4% copper, and the alumina coating (which contains incorporated chromium oxide) has good resistance to wear as well as corrosion. It also has the property of acting as a mordant for dyes, and articles so treated may receive coloured finishes by immersion in suitable dye solutions; alternatively the protection may be reinforced by lanoline or varnish, for which the coating provides an efficient bond. An advantage of the anodic as compared with cathodic methods of protection is that whereas large and inaccessible areas can readily be made anodic, there is great difficulty, as already pointed out (p. 387), in rendering a large area effectively cathodic. More recently other anodic processes have been introduced with the more particular object of increasing the intensity of the colours for decorative purposes, but this object is achieved at the expense of somewhat reduced efficiency on account of the increased porosity of the coating. These processes depend on the use of two main alternative electrolytes, solutions of sulphuric and oxalic acids respectively ("Alumilite" and Eloxyl processes). Duplex baths containing chromic acid are also used; other patented processes employ small amounts of inorganic salts for the production of coloured or black coatings. The treatment is followed by application of "sealing compounds" for the purpose of fixing the colour and increasing resistance to corrosion.

Corrosion products other than oxide films are not often sufficiently protective to warrant their stimulation by artificial methods. The green patina on copper is exceptional, and here the desire for the rapid production of the patina arises also from its æsthetic value and the long period of some 10 or 20 years normally required for its development. An interesting artificial method (Vernon, J. Inst. Metals, 1932, **49**, 153; *see also* Freeman and Kirby, Metals and Alloys, 1932, **3**, 190) is that in which the specimen is made the anode in an electrolytic bath kept at 95°C. and containing magnesium sulphate and hydroxide, with potassium bromate as oxidising agent. In as short a time as 15 minutes (or even sooner with appropriately high current density) a green patina is produced, which, however, at first consists of a basic sulphate, $CuSO_4{\cdot}Cu(OH)_2$, analogous with malachite. On subsequent exposure, the colour is maintained, whilst the basicity increases in a similar manner to that of the natural patina (*supra*). A further method (Vernon and Stroud, B.P., 1938, under Department of Scientific and Industrial Research), consisting of spraying the surface with thionyl chloride or other chlorine derivative of sulphuric acid, has the advantage that it can be applied *in situ* to a surface already blackened by exposure.

More commonly, nature is imitated in the spirit rather than the letter by the development of a reaction product which, whilst protecting the underlying metal, finds no counterpart in any natural process. Such, for example, is the case with the various *phosphate coatings* on iron and steel. These originated in 1906 in the process of Coslett (Birmingham), whereby the articles were treated in a hot solution of phosphoric acid to which iron filings were added. "Parkerising," employing a solution of iron and manganese phosphates, gives a protective and decorative (blackish) coating having many practical applications. "Bonderising" (much used in the automobile industry) is similar, but the bath contains substances that greatly speed up the reaction and the coating is used mainly for increasing the adhesion and permanence of a subsequently applied paint or varnish.

The protection of *magnesium* and *magnesium alloys*, of importance in aeronautical construction, is limited almost entirely to chemical methods, with or without the subsequent application of paint. The "I.G. chromate dip" employs a hot solution of sodium dichromate in nitric acid, producing a yellowish iridescent film, the protective value of which is limited. A development of this is the alum-dichromate process of Sutton and Le Brocq (J. Inst. Metals, 1931, **46**, 53; 1935, **57**, 199). The selenising process of Bengough and Whitby (*ibid.* 1932, **48**, 147; Trans. Inst. Chem. Eng. 1933, **11**, 176; D.S.I.R. Rep. Chem. Res. Board, 1934–7, London, H.M.S.O., 1938) involves immersion of the metal for a few minutes in a solution of selenious acid or acidified sodium selenite and produces a surface film of selenium which has considerable self-healing properties. Under test with sea-water spray the difference in behaviour between coated and blank specimens is spectacular, for the latter may disappear entirely whilst treated specimens remain comparatively unaffected. In both the alum-dichromate and the selenium processes (both of which are covered by British patents) the coating appears to find its most promising application as a base for paints.

Reference (Natural and Artificial Films).—E. S. Hedges, "Protective Films on Metals," 2nd ed., Chapman and Hall, London, 1937.

Paint and Allied Coatings.—The preservation of iron and steel by means of paint, for which, according to Jordan and Whitby (*infra*) some 40 million gallons of paint are used annually in Great Britain alone, involves many factors associated both with the paint and with the metal. A paint system is complex and its components—pigment, vehicle, thinner and drier—are interdependent in their contributions to the properties of the whole. It is usual, however, to classify protective paints according to the effect which the pigment may be expected to have *per se* on the corrosion of iron. Three types may be recognised, according as corrosion is likely to be (1) inhibited, (2) unaffected, (3) stimulated, by the pigment alone.

Characteristic examples of inhibitory pigments are provided by chromates (*e.g.* basic lead chromate, zinc chromate) and in this case the mechanism almost certainly resembles that of similar inhibitors in immersed corrosion, tending to render the iron passive. They are most usefully employed as "priming paints," in immediate contact with the metal. By far the most widely used primer is red lead, but here the passivating effect is probably supplemented by the formation, by reaction with the linseed oil, of lead compounds of high molecular weight which serve to cement the particles of pigment together. In practice, litharge normally present in commercial red lead is mainly responsible for this reaction. "Non-setting" red lead, having the minimum content of litharge, has been deprecated for corrosion-protection, particularly of ships' hulls (A. McCance, Trans. Inst. Eng. Scotland, 1936, 333); on the other hand, J. C. Hudson states (Proc. Chem. Eng. Group, S.C.I. 1937, **19**, 32) that satisfactory results have been obtained from non-setting red lead in the Iron and Steel Institute Corrosion Committee's tests. Probably the desideratum is a compromise in which the optimum proportion of inhibitory and setting capacity (depending on the type of work to be protected) shall be retained. For many purposes red lead may be safely diluted by the addition of varying proportions of inert "extenders," *e.g.* barytes, or asbestine.

Priming paints usually need to be reinforced by a top coating either for the purpose of healing mechanical defects in the undercoat or by effecting a more efficient exclusion of the surrounding liquid or atmosphere. For this purpose pigments of either groups (2) or (3) may be used. Red iron oxide is used extensively and confers good durability. Intrinsically neutral in character it may function either as an inhibitor or stimulator according as it is associated with alkaline or acid impurities from its manufacture. Recent developments include the use of red iron oxide with red lead or zinc chromate (mixed pigment) to give a combined priming and finishing coat. White lead (basic lead carbonate) and zinc oxide have mild inhibitive properties, but are more appropriately included with pigments of the second class; excellent as finishing coats for many purposes, they should not be used as primers where corrosion conditions are severe. The essentially chemical and physical mechanisms underlying protection by red lead and red iron oxide have been shown by laboratory experiments (Lewis and Evans, J.S.C.I. 1934, **53**, 29) and by field tests (Britton and Evans, J.S.C.I. 1932, **41**, 215); they have also been demonstrated by an electrochemical method (time-potential curves) by Burns and Haring (Trans. Electrochem. Soc. 1936, **69**, 169).

Pigments of the third class include such substances as graphite and certain metallic (*e.g.* bronze) pigments, which, on account of their cathodic nature, cannot normally be employed in direct contact with the metal. Their value lies either in their good weathering properties or in their ability to exclude moisture, and hence they are employed with advantage as finishing coats. In the case of graphite, exclusion of moisture is due largely to the "flakey" nature of the particles, the flakes lying on the surface with their long axes parallel to the metal. This property is also possessed by micaceous iron ore, a neutral pigment that is stated to be specially resistant to tropical conditions. Aluminium in the metallic condition might be expected to undergo "sacrificial corrosion" in contact with iron, but in practice the particles are probably sufficiently oxidised to render them neutral in character; they also have the advantage, to an even more marked extent than graphite, of a "flaky" or "leafy" nature. Metallic lead pigments are relatively inert and are highly durable under most conditions.

Of available media, linseed oil is by far the most widely used. Heat-treatment of the oil reduces the permeability of the paint film to water vapour and also its liability under certain conditions to act as a depolariser for nascent hydrogen and hence to facilitate corrosion. Moreover, the alkali reproduced at cathodes during corrosion in salt solutions is more likely to produce " alkaline peeling " of the paint film if raw, and hence more saponifiable oil is employed. Permeability to water vapour may be still further reduced by the addition of certain gums, waxes or resins. For special purposes, where high permeability to water is required, tung oil may be wholly or partially substituted for linseed oil. For most oil paints there is probably an optimum ratio between medium and pigment content (J. N. Friend, J. Oil Col. Chem. Assoc. 1922, **5**, 276), but if the pigment is inhibitive (*e.g.* red lead) rather than non-inhibitive (*e.g.* red iron oxide) lower proportions are permissible without detriment to corrosion-protection (Britton and Evans, J.S.C.I. 1932, **51**, 211T). Jordan and Whitby (*infra*) recommend, however, even with inhibitive primers, a pigment concentration as high as is consistent with penetration of the paint into all crannies and irregularities. The proportion of " thinner " (if this is the usual turpentine or alternatively white spirit) is important from the corrosion protection stand-point probably only in so far as it controls the thickness of the resulting paint film. " Drying "[1] of the linseed oil in a paint film is catalysed by the " drier " (certain compounds of lead, cobalt, or manganese) of which no more should be used than is necessary to ensure the drying of the paint within a reasonable time, depending on the conditions of exposure. A greater proportion of carefully selected driers is usually employed in paints for under-water service (*see* under " Corrosion of Metals—Corrosion of Ships' Hulls," *supra*).

The preparation of the metal surface previous to painting is of greatest importance. If the paint coating is to have maximum life, all mill-scale or rust should be removed. The danger of mill-scale is its liability to peel on exposure carrying with it *en bloc* the overlying paint. As, however, the scale is itself intrinsically resistant, there is hope of progress in the production of a thin scale that will have no tendency to peel. The danger of rust lies in its hygroscopic and adsorptive character. If electrolytes are present on the surface beneath the paint film this may act as a membrane through which moisture may pass osmotically from outside, even though the paint may be thoroughly dried before exposure (Bartell and Van Loo, Ind. Eng. Chem. 1925, **17**, 1052). Removal of scale may be effected (1) naturally, by weathering, (2) mechanically, by sand blasting (wire-brushing is more suitable for the removal of rust), (3) chemically, by pickling processes. Insufficient weathering often causes trouble, since the flaking of residual scale may continue after the paint is applied. Sand blasting has certain limitations, but has the obvious advantage of rapidity. J. C. Hudson (Vth Rep. Corr. Ctte. Iron and Steel Inst. 1938) states that pickling, as compared with partial weathering and careful hand-cleaning, increased the life of paint films by more than 150%. Pickling is usually carried out in a hot dilute solution of either hydrochloric or sulphuric acid, preferably the latter, with the addition of an inhibitor for the purpose of confining the attack to the scale and protecting the metal itself. Adequate washing, preferably in water containing alkali, should follow pickling. The use of phosphoric acid, at suitable dilution and temperature, has been advocated on the grounds that it leaves a film of basic iron phosphate, which increases the adhesion of paints, and washing may then be dispensed with. Alternatively, scale may be removed by the cheaper sulphuric acid, and a smaller amount of phosphoric acid applied after an intermediate washing (H. B. Footner, Vth Rep. Corr. Ctte. *ibid.* 369). In any case the surface should be thoroughly dry before painting is commenced. Moreover, adequate time should be allowed for any coat of paint to " dry " or set before the succeeding coat is applied. The foregoing remarks have referred particularly to iron and steel surfaces. The painting of non-ferrous metals may present special considerations, usually in the direction of providing a suitable chemical bond to ensure the adhesion of the paint; certain available methods have been discussed above. Trouble is frequently experienced in the painting of galvanised surfaces (hot-dipped zinc coatings); this may be overcome either by a preliminary weathering of the sheets, or by a suitable etching treatment (Vth Rep. Corr. Ctte., *ibid.* 303); *see also* " Hot-dipping Processes", p. 396.

Grease Coatings and Slushing Compounds.—For the temporary protection of iron and steel articles, machine parts, etc., during fabrication or storage, coatings of grease are employed which may subsequently be removed by an organic solvent. For this purpose lanoline is especially efficaceous and is usually employed in the form of solution in white spirit or solvent naphtha, the evaporation of which leaves the grease film uniformly distributed. Alternatively the grease may be applied in the form of an emulsion with an aqueous solution of sodium dichromate, or even with soap solution, such mixtures being generally known as " slushing compounds."

References (Paint Coatings).—Jordan and Whitby, " The Preservation of Iron and Steel by Means of Paint," 1936, Research Association of British Paint, Colour, and Varnish Manufacturers, Sixteenth Bulletin; L. A. Jordan, " The Preparation of Metal Surfaces for Painting," Chem. and Ind. 1937, **56**, 361. (For Protection of Ships' Hulls, including Anti-Fouling Preparations, *see* CORROSION, GENERAL, p. 382, 383).

Lacquers and Varnishes.—For protection against tarnishing of polished surfaces, *e.g.* of copper and silver and their alloys, transparent films of lacquer or varnish are employed. Formerly a natural resin (usually shellac) was the invariable component; in a " lacquer " this was dissolved in a volatile solvent (*e.g.* methylated spirit) the rapid evaporation of which yielded a film dry to the touch very quickly after application; in a " varnish " the medium was a drying oil (incorporated by heat-treatment) the setting of which occupied a much longer time, the resulting film, however, being tougher and more elastic. Whilst this distinction between a lacquer and a varnish is still roughly true, natural resins are now very largely supplemented by a wide range of so-called synthetic resins. (For detailed information, *see* " Synthetic Resins and Allied Plastics," by Barry, Britton, Langton, and Morrell, London, Oxford University Press, 1937. Also " Modern Developments in Plastics," by Sir Gilbert Morgan, Chemistry and Industry, 1937, **56**, 103). These were at first of phenol formaldehyde type, available only in the form of the simple spirit solution (*e.g.* " Novolak ") but many types of oil-soluble resins are now employed in the manufacture of protective varnishes. Certain of the modified phenolic derivatives find use in protecting metal surfaces against industrial fumes. They are also used as stoving lacquers for the protection of tinplate against acid juices, their freedom from odour and taste rendering them particularly valuable for the purpose. A. F. Brockington (J. Electrodepositors' Tech. Soc. 1937, **12**, 133) states, however, that the modified alkyd types of phenol aldehyde resins are seldom used in the unpigmented state on metals since they have an acid reaction and tend to tarnish copper and brass during stoving. Other oil varnishes employing synthetic resins (*e.g.* those obtained from polystyrene and coumarone) have good alkali-resisting properties.

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[1] For the chemistry of the drying process and of paints generally articles on " Paint " should be consulted.

" Cellulose lacquers " consist usually of a solution of cellulose nitrate in a mixture of solvents (amyl acetate, etc.), but in modern practice either natural or synthetic resin is usually incorporated for the purpose of improving the adherence and gloss of the dried film. The mixture also includes, in common with other " cold lacquers," a certain proportion of higher alcohols, their function being to prevent too rapid volatilisation of the solvent with consequent " blooming " or " blushing " of the film; this term refers to a defect caused by precipitation of moisture when a lacquer is applied under humid conditions. Cellulose lacquers, commonly applied by spraying, are particularly suited for highly polished surfaces. Both cellulose and gum lacquers may be tinted with suitable dyes. The varnish-like nature of certain invisible oxide films (p. 392) may be recalled; it has been suggested (Vernon, Res. Rep. Brit. Non-ferrous Met. Res. Ass., Nov. 1927, 9) that the production of such films by heat-treatment (*e.g.* on brass) might with advantage precede the application of lacquer, thus reinforcing the protective effect (partly by providing a better chemical " bond ") whilst retaining the natural colour of the original surface. The application of lacquers and varnishes to thicker (visible) films produced by chemical treatment is common practice; they may either supplement the protective effect of the primary coating (*e.g.* protection of aluminium and magnesium alloys, p. 392) or they may serve to protect a decorative coating (as produced in certain metal-colouring processes) which itself may have little protective value.

The lacquering or varnishing of tinplate for food containers has for its object not so much the supplementing of the protection of iron by tin as the suppression of certain reactions between tin and fruit juices which may cause either blackening of the tin or discoloration of the juice. Indirectly, indeed, the lacquer coating, if imperfect, may lead to local attack on the tin, and by concentrating the attack at the weak places may bring about the perforation of the container. Walker and Lewis (J. Ind. Eng. Chem. 1909, **1**, 754) suggested that in such cases a varnish film might, by acting as a hydrogen acceptor, facilitate the depolarisation of hydrogen even in the absence of oxygen and so accentuate the anodic attack on the adjacent bare places. Morris and Bryan (D.S.I.R. Food Investig. Reps. 1933, 145) conclude that the lacquer film in modern practice is inert although the tin coating beneath may play some part electrochemically. They recommend (*ibid.* 1935, 169) supplementing the usual pre-fabrication lacquering of the tinplate with a final lacquering of the can interior with a quick-stoving lacquer.

Chlorinated rubber has within recent years received considerable attention as a protective coating (G. Schultze, Korr. u. Metallschutz, 1936, **12**, 249; J. P. Baxter, Chem. and Ind. 1936, **55**, 407). In the form in which it is typically applied—a solution in xylene or other solvent with incorporated plasticisers such as certain chlorinated hydrocarbons—it is analogous to a synthetic resin lacquer. Pigments may, however, be added, with or without a proportion of drying oil (*e.g.* tung oil) and hence certain mixtures resemble oil paints. The essential feature of the chlorinated rubber coating, besides its high elasticity, is its capacity of giving a high resistance to chemical attack, both acid and alkali; it appears to be well suited for under-water protection, particularly under tepid conditions, as in thermostats, etc.

Bituminous Coatings.—The simple " bituminous paints " are not true paints as previously defined. They consist of either natural asphalt or pitch (petroleum residual or coal tar) dissolved in a volatile spirit (*e.g.* white spirit, solvent naphtha, etc.) so that drying, as distinct from the " drying " of an oil paint, consists merely in the evaporation of the solvent. Such bituminous coatings afford good protection to iron and steel, sometimes under conditions such as would be deleterious to ordinary oil paints (*e.g.* atmospheres polluted by chemical fumes); they are, however, adversely affected by excessive sunlight. They are widely used for structural work, for which purpose they are improved both aesthetically and in durability by pigmentation, particularly with aluminium powder. Excellent results, for example, have been quoted for the use of tar paints containing 12 to 15% aluminium (Vth Rep. of Corr. Ctte., Iron and Steel Inst. 1938, 320); the aluminium floats to the surface of the film which, when dry, has practically the same appearance as an aluminium paint proper. A modification of bituminous paint, using bitumen together with drying oil additions, the coating being " stoved " after application, results in black " japan." For the protection of pipelines underground, coal-tar pitch, the basis of the well-known " Angus Smith compound," is extensively employed. The original patent (1848) specified the use of linseed oil as an addition to the pitch to obtain the right consistency and elasticity. In modern practice the pipes are heated and immersed in the molten bath of refined coal-tar pitch (sometimes with certain " filler " additions) and frequently the coating is reinforced with hessian or similar material. Damage to this protective coating in transit from the mill to the trench may result in local failures in service. For marine conditions, J. N. Friend (D.S.I.R. " Deterioration of Structures in Sea-water," XVth Rep. Ctte. Inst. Civ. Eng. 1935, 85) reports excellent results from the use of coal-tar coatings on iron and steel, and states that coal-tar from horizontal retorts was superior to that from vertical retorts, whether applied hot or cold; it was improved by the addition of slaked lime (*see also* " Corrosion and Protection of Ships' Hulls," p. 382). " Bituminous Materials in Paint " have been surveyed by L. A. Jordan (Res. Assoc. Brit. Paint Manufac. 14th Bull. 1935); *see also* Jordan and Whitby, 1936, *supra.*

Metal Coatings.—The non-ferrous metals most commonly applied in the form of thin coatings for the protection of iron and steel are aluminium, lead, tin, and zinc. Methods of application include either purely metallurgical processes (rolling, hot-dipping, cementation, spraying) or electro-deposition.

" *Rolled-on* " *Coatings.*—In the " old Sheffield plate " process (rendered obsolete by the introduction of silver plate) thin sheets of silver were beaten on to copper, the operation being assisted by heat. Within recent years the principle has been revived in " metal-cladding " processes. Thus, copper-clad and nickel-clad steels are produced by rolling or drawing a heated billet of steel " sandwiched " between plates of the protecting metal. Aluminium-clad steel has been proposed as a substitute for tinplate in the canning of foodstuffs. A promising development is the rolling of a veneer of stainless steel on to an ordinary steel base. Aluminium alloys of the duralumin type (having high strength but a susceptibility to intergranular corrosion from which the weaker aluminium is free) are similarly covered with pure aluminium. The duplex material (American " Alclad," British " Aldural," German " Allautal ") is used extensively in aircraft. Alternatively (as in " duralplat "), a relatively resistant silicon-aluminium alloy (free from copper) may be used for the outer layer, the rather less resistance to corrosion being compensated by the greater resistance to wear.

Hot-Dipping Processes.—Hot-dipping is employed principally for coating iron and steel with tin or zinc (tinplate and " hot-galvanising " industries). In each case the bond with the underlying metal is provided by a certain amount of alloying. Exceedingly thin on tin, the alloy layer reaches much grosser dimensions on zinc, where two and occasionally three intermediate layers can be detected, each characterised by an intermetallic compound. Advantage is claimed for a process of subsequent annealing for the purpose of removing mechanical weakness set up by the presence of these layers. In all cases scale adhering to the metal must be completely removed by pickling prior to the hot-dipping. The composition of both basis and covering metal is usually more rigidly controlled for tinplate than for galvanised iron. Metallic additions, for example, are not normally made to the tin bath, but to the zinc bath very small quantities of either aluminium or tin are commonly made with the object of increasing the fluidity of the bath or improving the appearance of the coating. Tinplate finds its widest application in the manufacture of food containers and dairy utensils, whilst galvanised iron is used for roofing and for much large-scale work exposed to the open air. (Hot-tinning is also applied to copper articles, particularly water-pipes and cooking utensils.) Tin and zinc are normally cathodic and anodic respectively to iron (*see* " Electro-potential Series," Table III, p. 376). Hence, in the event of the underlying metal becoming exposed at any point, in the presence of a suitable electrolyte, the iron in contact with tin is attacked preferentially, leading to perforation of the sheet, whilst a zinc coating, under similar conditions, will undergo " sacrificial corrosion " where the underlying metal is exposed and thus protect it from attack. Circumstances sometimes arise, however, in which a reversal of polarity takes place, as, for example, with tinplate in the presence of certain fruit juices. It is important that a certain minimum thickness of coating should be exceeded if a reasonable life is to be assured. This is a general rule that applies to all metallic coatings, which frequently depend for their corrosion resistance on the ability to build up a protective film in the particular environment in which they are placed. This normally involves an initial period during which the coating itself is contributing to the formation of the protective layer, and its initial thickness should thus be at least sufficient to survive this interim period. This applies equally to coatings of the anodic type, since the conditions which result in " sacrificial " corrosion, and hence loss of the protective coating, should be avoided.

Galvanised iron, when used for structural work exposed to the open air, is frequently further protected by painting. The unsatisfactory adherence of paint to the galvanised coating may be overcome by a preliminary period of weathering; various solutions (*e.g.* oxalic acid), are also employed for etching the freshly deposited coating prior to painting (*see* p. 394).

Terne plate consists of iron or steel sheet coated (by hot-dipping) with a lead alloy containing 10 to 25% tin. (Lead itself does not give a satisfactory hot-dipped coating on steel owing to the absence of any alloy " bond.") It is largely used for roofing as a substitute for lead sheet or galvanised iron, but painting is usually necessary; this is facilitated by the readiness with which paint adheres to the material without any preliminary treatment.

Cementation Processes.—The principal cementation process (heating of the previously cleaned basis metal with the coating metal, the latter in powdered form, usually " diluted " with oxide) is that of " sherardising," due to the late Sherard Cowper-Coles, in which iron or steel is coated with zinc. The process is particularly suited for small articles, such as bolts, nuts, screws, for which it has the advantage over hot-dipped coatings in respect to a considerably smaller dimensional change. The coating differs principally from the hot-dip coating in that there is usually only one alloy layer, whilst the outer layer of pure zinc is often not represented at all. It is in the uniformity and continuity of the alloy layer that the corrosion resistance of sherardised coatings principally depends. This alloy is normally anodic to iron but less so than zinc.

The analogous process of cementation by means of aluminium (calorising) is used more particularly for protection against oxidation at high temperatures, where the protection is due to the refractory properties of the film of alumina. The coating is also useful for protection against sulphurous fumes.

Metal-spray Processes.—The process devised by Schoop in 1910, whereby a spray of finely divided metallic particles is ejected from a blowpipe or " pistol," has within recent years assumed important industrial dimensions. Metal wire is supplied to the pistol, in which it is melted at the tip by an oxyacetylene flame, atomised by excess of gas, and carried forward at a relatively low temperature (actually below the ignition point of a match). Adhesive deposits of various metals may be sprayed on to steel, which should be previously sand-blasted to obtain the necessary " keying," since no appreciable alloying occurs. An obvious advantage of the method is its ability to apply a protective metal coating to structures, *in situ.* Recent modifications, as the Schori processes, have aimed at increasing the speed of working by supplying metal powder to the pistol instead of wire ; this process also sprays metal/glass mixtures which are claimed to provide flexible coatings of metal silicate resistant to sea-water attack. Marked resistance to corrosion in industrial and marine atmospheres has been obtained by the spraying of thin coatings of aluminium on steel by the ordinary method, particularly when the coatings have been subsequently treated with cellulose lacquer (W. E. Ballard, Trans. Manch. Assoc. Eng. 1935, 113). The possibility of using sprayed metal coatings for the protection of ships' hulls is referred to in the Fifth Report to the Iron and Steel Institute Corrosion Committee (*l.c.*, 219).

Electro-deposited Coatings.—Much research has been carried out with the view to increasing the efficiency of electro-deposition processes, by which a wide range of protective metal coatings are now produced. It has been shown that interalloying of coating and base does not take place, although in certain cases slow diffusion may occur subsequent to deposition. On the other hand, the relationship may be so intimate that the lattice of the basis metal may be continued and the structure exactly copied by the deposit (A. W. Hothersall, Trans. Faraday Soc. 1935, **31**, 1242).

Electro-deposition has the advantage of producing a uniform coating under controlled conditions with little dimensional change. It is particularly suitable for small articles of irregular shape, but for special purposes may be applied to large-scale work. Small articles are frequently plated in bulk by the " barrel " method ; a rotating barrel dipping into the electrolyte contains the articles, the mutual contact of which ensures electrical connection and provides a certain burnishing action which improves the appearance of the deposit.

Zinc coatings are produced commercially by each of the four main methods ; the term " galvanised " iron, however, almost invariably refers to the " hot-dipped " coating. Tin coatings are produced to a comparatively small extent by electro-deposition, which has, however, been recommended for supplementing the hot-dip process, the two operations yielding a coating that is practically free from pores.

Nickel-plating on iron and steel is carried out on the largest scale. Excellent protection against corrosion is afforded under many conditions, nickel coatings being particularly suited for parts of equipment which must resist both corrosion and abrasion. In atmospheres containing traces of sulphur dioxide, provided a critical relative humidity of approximately 70% is exceeded, the polished surface undergoes a characteristic filming or " fogging " (*see* General article under Atmospheric Corrosion). In modern practice nickel coatings are covered, for decorative purposes, with a film of electro-deposited chromium. This resembles nickel in its extreme hardness and resistance to wear, fine appearance, and ability to take a high polish, but has the advantage of freedom from fogging. (Small amounts of chromium alloyed with nickel also inhibit fogging, but the two metals cannot, as yet, be deposited simultaneously.) An analogous recent development is the plating of a thin film of rhodium on electro-deposited silver. This retains the advantages of silver plate with freedom from tarnishing, to which unprotected silver is characteristically liable in atmospheres containing traces of sulphur compounds.

The use of electro-deposited cadmium is increasing considerably. Whilst it appears to have no appreciable advantage over zinc for open-air conditions, its whiter and pleasanter appearance, particularly when polished, is advantageous for indoor purposes, as in electrical and radio parts. In the Udylite process, iron articles, after electroplating with cadmium, are heated at 150° to 200° for several hours.

Arising from difficulties in producing coatings of lead by other methods (*e.g.* absence of alloying in hot-dip and cementation processes and health hazards in spraying processes) developments have recently taken place in the large-scale electro-deposition of lead on iron for roofing and constructional purposes (F. W. Hay, Metallurgist, 1937, **11**, 23). High resistance to industrial atmospheres is brought about by the formation of a surface film of insoluble lead sulphate. Developments in electroplating are surveyed by

S. Wernick (Chem. and Ind. 1934, **53**, 948; Ind. Chem. 1935, **11**, 233). *See also* works recommended below.

TESTING OF METALLIC COATINGS.—Many methods are in use for testing soundness, thickness, and adhesion of metal coatings. One of the earliest schemes for detecting pinholes was by means of the ferroxyl indicator of Cushman and Walker. This is prepared by the addition of a little potassium ferricyanide and phenolphthalein to a dilute solution of sulphuric acid ; a convenient method of carrying out the test is to use a test paper saturated with the reagent, which is pressed on the surface. In the case of a cathodic coating (*e.g.* nickel on iron) the position of the pinholes is indicated by a blue spot of ferrous ferricyanide where iron passes into solution. For tinplate, Macnaughtan, Clarke, and Prytherch (J. Iron and Steel Inst. 1932, **125**, 159) recommend a solution containing sodium chloride with potassium ferricyanide ; they also obtain excellent results from a simple " hot water test," observing suitable precautions. Pinholes in anodic coatings (*e.g.* zinc on iron) are more difficult to demonstrate, but usually they are of less consequence in practice. The thickness of zinc deposits on iron is still determined by the old established Preece test ; this consists in repeated immersion of the samples (usually galvanised wire) in copper sulphate solution at one minute intervals, the number of immersions required to produce a deposit of copper on the basis metal giving an indication of the thickness of the coating. A number of methods have been proposed for overcoming certain objections to the Preece test. Britton (J. Inst. Metals, 1936, **58**, 211) makes the sample the anode of an electrolytic cell at a fixed current density and notes the time taken to remove the coating from a given area. The thickness of tin coats on iron is determined rapidly by Clarke by removal in a solution of hydrochloric acid and antimony chloride, the latter preventing attack on the iron. In the " B.N.F. jet test " the thickness of the coating at any desired point is determined by measuring the time required for perforation of the coating by a jet of an appropriate solution which is allowed to impinge on the surface at a constant pressure. It is applicable to a wide range of coatings (S. G. Clarke, J. Electrodep. Tech. Soc. 1936, **12**, 157; 1937, **12**, 1–18). Methods of testing zinc coatings have been comprehensively surveyed by L. Kenworthy (J. Inst. Metals, 1937, **61**, 143).

References (Books dealing with Metal Coatings): H. S. Rawdon, " Protective Metallic Coatings," Chemical Catalog Company, New York, 1928; H. Bablik, " Galvanising," 2nd ed. (English translation), E. & F. N. Spon, London, 1936; E. S. Hedges, " Protective Films on Metals," 2nd ed., Chapman and Hall, London, 1937.

W. H. J. V.

CORROSIVE SUBLIMATE. Mercuric chloride.

CORUBIN. An artificial corundum (*v.* ABRASIVES and CORUNDUM.)

CORUNDUM (Fr. *Corindon* ; Ger. *Korund*; from the Hindi *kurund*, Sanskrit *kuruvinda*). Crystallised alumina (Al_2O_3). The crystals belong to the rhombohedral system, and are isomorphous with hæmatite (Fe_2O_3). They vary considerably in habit, having the form of hexagonal prisms, pyramids, or tables. In some crystals the combination of six faces of the primary rhombohedron with two faces of the basal pinacoid produces a form strikingly similar to the regular octahedron. There is no true cleavage, but often the crystals and crystalline masses show a pseudo-cleavage or parting parallel to the basal plane or to one or more faces of the primary rhombohedron, due to lamellar twinning on these planes. On these surfaces the lustre is sometimes pearly, but otherwise it is usually vitreous, or inclining to adamantine in character. The fracture is uneven to conchoidal ; and the sharp jagged edges of the irregular grains give effect to the cutting power of the material when used as an abrading agent. Analyses show the presence of 95–99% of alumina, with small amounts of ferric oxide, magnesia, silica, water, etc., and sometimes traces of chromium. Sp.gr. 3·9–4·1. The crystals are optically uniaxial and negative ; refractive indices for sodium-light ω 1·768, ϵ 1·760. The dichroism is marked. Next to diamond, it is the hardest of minerals, being placed as No. 9 in the scale of hardness ; on this account it was formerly known as adamantine spar.

A distinction is made between the transparent " precious corundum " and the dull, opaque " common corundum," while a third still less pure variety is known as emery (*v.* ABRASIVES). This division also corresponds with the economic uses of the mineral, " precious corundum " being used for gem-stones, and " common corundum " and emery for abrasive purposes. The pure, well-crystallised material is perfectly colourless and transparent with a high degree of brilliancy. Traces of inorganic impurities, however, produce a wide range of colours, which are more vivid in the stones of gem-quality, namely red (ruby), orange and yellow (" oriental topaz "), green (" oriental emerald "), blue and indigo (sapphire), and violet (" oriental amethyst "). Although such names are in popular use for jewellery, this mineral has, of course, no relation to topaz, etc. Parti-coloured stones are not uncommon. The colour of common corundum is usually grey or brown.

Corundum is not a widely distributed mineral, but it is found in abundance at certain localities. It occurs in igneous and metamorphic rocks in which no free silica is present as quartz, such as syenite, gneiss, peridotite, and serpentine, and in crystalline limestones. Material of gem-quality is usually collected as water-worn pebbles in gravels derived from these rocks. Material for gem-stones and that for abrasive purposes are not, as a rule, mined in the same localities. Taking first the localities for the gem-varieties, the following may be noted as a few of the most important. The best rubies are obtained from the famous mines near Mogok in Upper Burma, where they occur in a white crystalline marble near its contact with gneiss ; they are mined in the detrital deposits derived from this rock. Dark-coloured rubies are obtained with sapphire from alluvial deposits in the provinces of Chantabun and Krat in

Siam. Stones of good quality have also been mined together with common corundum in Macon Co., North Carolina. The best sapphires come from the gem-gravels of Ceylon ; other localities of importance are Siam and Kashmir. Dark blue and greenish-blue sapphires occur abundantly in gravels near Anakie in Queensland ; while paler stones of various shades (" fancy stones ") are plentiful in the neighbourhood of Helena in Montana.

Common corundum as used for abrasive purposes (apart from emery) was formerly mainly mined in the United States ; later the Canadian and South African deposits came into prominence ; while now the latter are being ousted by the artificial products carborundum and alundum. India has also since remote times produced a certain amount which has been largely used by the native lapidaries. In the United States the corundum deposits extend along the Appalachian Range from Alabama to Massachusetts, reaching their greatest development in North Carolina and Georgia. Here they occur in peridotites near their contact with gneiss. In Canada a belt of corundum-bearing syenites (nepheline- and related alkali-syenites), associated with the Laurentian gneisses, extends for 100 miles across Renfrew, Hastings and Haliburton counties in Ontario, the principal mining district being near Craigmont in Renfrew Co. Large rough crystals of corundum are abundant in gneiss in Madagascar and at Steinkopf in Namaqualand, South Africa. More recently, important deposits have been discovered and worked in the Zoutpansberg and Pietersburg districts in northern Transvaal.

The corundum-bearing rock as mined is crushed between hardened steel rolls and the heavier corundum separated in water by means of jigs and concentrating tables. It is sifted into different grades of fineness and used (1) as loose grains ; (2) mixed with glue or other soft cement as a coating on paper or cloth ; and (3) as corundum-wheels for grinding. The last-named are of three classes : (*a*) The " vitrified wheel," in which the corundum is mixed with clay and baked at a high temperature, with the result that the grains of corundum are set in a matrix of porcelain. (*b*) The " chemical wheel," in which sodium silicate is the binding material. (c) The " cement wheel " with shellac, rubber, linseed-oil, etc., or magnesium oxychloride. Another use for corundum, depending on its hardness, is for the pivot supports for watches (watch-jewels) and other delicate instruments, the poorer qualities of gem-material being used for this purpose. Although corundum is the richest ore of aluminium, there are difficulties in its use for the extraction of the metal. It has, however, been used directly in the preparation of aluminium-copper and aluminium-iron alloys.

The artificial preparation of crystallised corundum was first effected by M. A. Gaudin, in 1837, by decomposing potash-alum with charcoal. It has since then been produced by a variety of methods, and is now manufactured on a large scale both for use as gem-stones and for abrasive purposes. Beautiful crystals of ruby were prepared by E. Frémy and Feil, in 1877, by heating a mixture of alumina and red-lead with potassium dichromate in a porous fireclay crucible ; a fusible aluminate of lead was thereby formed, which was decomposed by the silica of the crucible with the separation of crystallised alumina. The crystals so obtained, though of some size, good colour, and perfectly transparent, were unfortunately too thin for cutting as gems. A far greater measure of success was achieved by A. Verneuil in 1902, who has produced fine gems of all colours. Interesting experiments from a petrological point of view were conducted by J. Morozewicz in 1898, in which he obtained crystallised corundum in silicate magmas supersaturated with alumina. Artificial corundum, used as an abrasive under the trade name of *alundum* (aloxite, adamite), is now manufactured on a large scale at Niagara Falls by fusing bauxite in an electric furnace. *Corubin* formed as a by-product in the Goldschmidt thermite process is also an artificial corundum.

References.—A. E. Barlow, " Corundum, its Occurrence, Distribution, Exploitation, and Uses," Canada, Dept. Mines, Geol. Survey, Mem. 57, Ottawa, 1915, 378 pp. (with special reference to the Canadian deposits) ; T. H. Holland, " Corundum," Manual of the Geology of India, 2nd ed., Calcutta, 1898 (with special reference to the Indian deposits) ; A. L. Hall, " Corundum in the northern and eastern Transvaal," Mem. Geol. Surv. South Africa, 1920, No. 15 ; G. P. Merrill, " The Non-metallic Minerals," 2nd ed., New York, 1910 ; J. H. Pratt, Bull. U.S. Geol. Survey, 1906, No. 269 ; J. H. Pratt and J. V. Lewis, North Carolina Geol. Survey, 1905, i. ; M. Bauer, " Edelsteinkunde," 3rd ed., by K. Schlossmacher, Leipzig, 1928–1932, and English translation, " Precious Stones," by L. J. Spencer, London, 1904 ; " Abrasives," Imperial Institute, London, 1929.

L. J. S.

CORYBULBINE *v.* Corydalis Alkaloids. Corydaline Sub-Group.

CORYCAVINE *v.* Corydalis Alkaloids, Corycavine Sub-Group.

CORYDALINE *v.* Corydalis Alkaloids, Corydaline Sub-Group.

CORYDALIS ALKALOIDS.—The corydalis species belong to the Fam. Papaveraceæ ; there are about ten different species known to contain alkaloids, of which *C. cava* (syn. *tuberosa*) is the most important (*v.* Wehmer, " Die Pflanzenstoffe," Jena, 1929, p. 388). For references to early chemical investigations, *v.* Ziegenbein (Arch. Pharm. 1896, **234** 492). The most important alkaloid corydaline was isolated by Wackenroder as early as 1826.

Extraction.—According to Gadamer (Arch. Pharm. 1902, **240**, 21) the finely ground corydalis roots are exhausted with 94% EtOH. The solvent is removed by distillation, the oily residue is acidified with acetic acid and diluted with H_2O. The aqueous solution is made alkaline with ammonia and extracted with Et_2O, when all alkaloids pass into the solvent except *corytuberine,* which is obtained by evaporating the mother-liquor. By concentrating the Et_2O-solution a first crystalline fraction (*a*) melting from 160–180° is obtained which contains *corydaline, bulbocapnine, corycavine,* and *corybulbine.* This mixture may be separated by successively extracting the crystalline mass with small amounts of boiling EtOH. The ethereal mother-liquor from (*a*) is then completely evaporated, when a fraction (*b*), melting from 130–140°, is obtained, which consists almost entirely of corydaline. The fraction (*b*) is converted into the hydrobromides, when first bulbocapnine·HBr separates; by fractional precipitation of the remaining hydrobromides with ammonia corydaline, corybulbine, iso*corybulbine, corydine,* and corycavine, and further amounts of bulbocapnine are obtained. The mother-liquors are acidified with HCl when further crystalline fractions are obtained. The residue is transformed into the rhodanides, from which by extraction with EtOH corycavamine rhodanide is left behind.

Gadamer's process is merely a general guidance and not an accurate prescription; it has often been modified if a special alkaloid was sought after. The separation and purification of the different alkaloids is a very tedious and laborious process; also the yields of the different alkaloids vary to a great extent.

Other investigated corydalis species are :

C. ambigua (Chinese C.) : Makoshi (Arch. Pharm. 1908, **246**, 381), Chou (A, 1928, 927 ; *ibid.* 1929, 477, 1085 ; *ibid.* 1933, 652 ; *ibid.* 1934, 1014). Huang-Minlon (Ber. 1936, **69**, [B], 1737) (important paper).

C. vernyi (Japanese C.) : Asahina and Motigase (J.C.S. 1921, **120**, I, 86).

C. decumbens : Makoshi (Arch. Pharm. 1908, **246**, 401) ; Osada (Amer. Chem. Abstr. 1928, **22**, 592).

C. lutea and *C. nobilis* : Schmidt (Arch. Pharm. 1908, **246**, 575).

C. aurea : Heyl (Apoth.-Ztg. 1910, **25**, 137) ; Eppson (Amer. Chem. Abstr. 1935, **29**, 2662).

C. solida : Haars (Arch. Pharm. 1905, **243**, 154).

C. ternata Nakai (Korean C.) : Go (Chem. Zentr. 1930, I, 234).

The arrangement of the corydalis alkaloids into three groups is due to Gadamer, Ziegenbein, and Wagner :

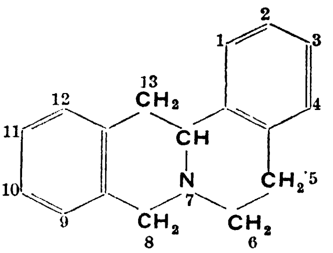
Group I : consists of weakly basic alkaloids, which are readily oxidised by iodine to berberine-like compounds (corydaline sub-group).

Group II : includes stronger bases which are attacked by iodine solution (corycavine sub-group).

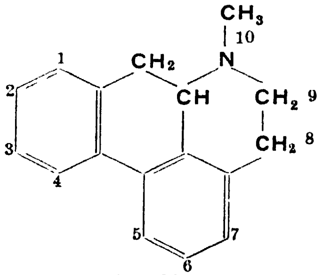
The alkaloids of Group II are closely related to cryptopine and protopine, and contain the characteristic ten-membered ring-system.

Group III : comprises the strongest bases of the series, these contain free phenolic hydroxyl groups and are easily oxidised by iodine (corytuberine sub-group).

Group III comprises alkaloids which belong to the *aporphine* group (*v.* Gadamer, Oberlin, and Schoeler, Arch. Pharm. 1925, **263**, 81). The numbering of the tetrahydroprotoberberine (Buck, Perkin and Stevens, J.C.S. 1925, **127**, 1462 ; Gadamer, Späth and Mosettig Arch. Pharm. 1927, **265**, 675) and the aporphine skeleton is the following :



Tetrahydroprotoberberine.



Aporphine.

Group I.—Corydaline Sub-group.—This comprises the weak alkaloids of the corydalis root, viz. corydaline, dehydrocorydaline, corybulbine, *iso*corybulbine, tetrahydropalmatine, and corypalmine. They have in common the property of being capable of oxidation with iodine to the dehydro-compounds which are quaternary bases closely related to berberine and palmatine.

Corydaline was first isolated from *C. cava* by Wackenroder (Berz. Jahr. 1826, **7**, 220), but it was Freund and Josephi who gave it the correct formula. The yields vary considerably, Martindale (Arch. Pharm. 1898, **236**, 215) gives 0·9%, Ziegenbein (Arch. Pharm. 1896, **234**, 497) quotes 0·57%.

Corydaline (I), $C_{22}H_{27}O_4N$, $[\alpha]_D^{20}$ +300° (in chloroform), m.p. 135°, crystallises from EtOH in colourless, short, six-sided prisms, sparingly soluble in cold, but easily soluble in hot EtOH, Et_2O, $CHCl_3$ and benzene, (I) contains 2 asymmetric carbon atoms ; it is slowly oxidised by atmospheric oxygen to the yellow dehydrocorydaline (II). For absorption spectra of (I) *see* Dobbie and Lauder (J.C.S. 1903, **83**, 605), Dobbie and Fox (J.C.S. 1914, **105**, 1639), and Girardet (J.C.S. 1931, 2630). (I) gives two *methiodides* : one being crystalline, m.p. 238–240°, $[\alpha]_D$ +139·4°, the other amorphous, m.p. 64–68°, $[\alpha]_D$ +110° (von Bruchhausen and Stippler, Arch. Pharm. 1927, **265**, 152).

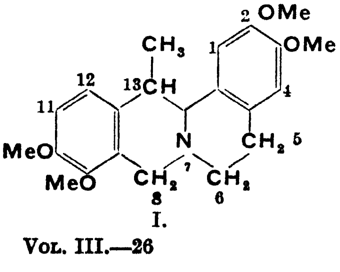
The salts of (I) are crystalline: $B\cdot HCl+2H_2O$, columnar crystals from H_2O, m.p. 206–207° ; B·HI, pale yellow prisms of indefinite m.p. ; $B\cdot HNO_3$, tablets from EtOH, m.p. 198°, sparingly soluble in H_2O ; B·HCNS columns from EtOH, m.p. 208° ; platinichloride, brown crystals, m.p. 227° ; the *ethyl sulphate* forms characteristic, large prisms, m.p. 152·5°.

By oxidation of (I) with iodine (Ziegenbein, Arch. Pharm. 1896, **234**, 505), bromine (Martindale, Arch. Pharm. 1898, **236**, 238) or very dilute

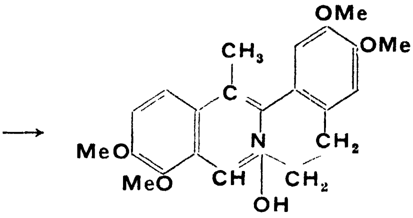
HNO_3 (Dobbie and Marsden, J.C.S. 1897, **71**, 657) *dehydrocorydaline* (II) is obtained, which is identical with a natural base isolated from *C. cava, vernyi, ambigua,* and *solida.* (II) is a yellow crystalline powder, m.p. 112–113° (decomp.), the salts are crystalline, $B{\cdot}HCl, 4H_2O$, yellow leaflets, soluble in H_2O and $EtOH$; $B{\cdot}HBr$, yellow needles, m.p. 126°; $B{\cdot}HI, 2H_2O$, small yellow needles; $B{\cdot}HAuCl_4$, red-brown needles from $EtOH—HCl$, m.p. 219°; $B_2{\cdot}H_2PtCl_66H_2O$, yellow needles from $EtOH—HCl$; (II) in solution is a quaternary ammonium base. In the free state it melts and decomposes at 112-113°, has the composition $C_{22}H_{25}O_5N$ and must be regarded as a ψ-base with the keto-composition containing the groups $\cdot CMeO$ and $NH<$ instead of $\cdot CMe{:}N{\cdot}(OH)<$ for it forms an oxime, orange-yellow crystals, m.p. 165° (Haars, Arch. Pharm. 1905, **243**, 171), it also unites with 1 mol. of $CHCl_3$ to form a colourless crystalline compound m.p. 162–163° and an amorphous acetone compound (Ziegenbein, *ibid.* 1896, **234**, 492).

By reduction of (II) with zinc and sulphuric acid *r-corydaline* (III) m.p. 134–135° and *r-mesocorydaline* (IV) m.p. 158–159°; m.p. 163–164°: Späth and Posega, Ber. 1929, **62**, [B], 1029) are formed, which are both optically inactive (Gadamer, Arch. Pharm. 1902, **240**, 19; *ibid.* 1916, **254**, 295). (IV) may be resolved into *d*- and *l*- forms by crystallisation of the *d*-camphorsulphonate, the *d*- form is not identical with natural (I) (Gadamer, *ibid.* 1902, **260**, 50 Haars, *l.c.*). (III) has not been resolved, but its sulphonic acid can be separated into *d*- and *l*- forms by crystallisation of the brucine salts, the *d*- form is identical with the sulphonic acid prepared from natural corydaline (Gadamer, *ibid.* 1916, **254**, 295).

Insight into the constitution of (I) has principally been obtained by oxidation experiments (*cf.* Dobbie and co-workers, J.C.S. 1897, **71**, 657; 1902, **81**, 145; Haars, *l.c.*). Oxidation with permanganate yielded hemipinic, *m*-hemipinic acid and corydaldine; HNO_3 gave rise to the intermediate oxidation products corydic, corydilic, and methylpyridine carboxylic acids respectively, and the ultimate products were pyridine-2:3:4:5-tetracarboxylic acid, hemipinic and *m*-hemipinic acids. Important contributions towards the final elucidation of the structure of (I) were made by Späth and Lang (Ber. 1921, **54**, [B], 3074), Gadamer and von Bruchhausen (Arch. Pharm. 1921, **259**, 245), Lawson, Perkin and Robinson (J.C.S. 1924, 631), and by von Bruchhausen and Stippler (*l.c.*). *Cf. also* Koepfli and Perkin (J.C.S. 1928, 2989) where short survey is given. The following constitution for (I) has been established:



I.



II.

Synthetical experiments were carried out by Pictet and Malinovski (Ber. 1913, **46**, 2688), Späth and Lang (*l.c.* 1921), and Späth and Mosettig (Annalen, 1923, **433**, 138), but they failed to give a product identical with (III) or (IV). F. von Bruchhausen (Arch. Pharm. 1923, **261**, 28) was able to introduce the C-methyl-group into position 13, and he obtained (III) melting at 135–136°; Späth and Holter (Ber. 1927, **60**, [B], 1891) obtained synthetic (III) and (IV) in connection with their work on corycavine. An interesting synthesis of (III) and (IV), starting from papaverine, was described by Späth and Kruta (Ber. 1929, **62**, [B], 1024).

Corybulbine and isoCorybulbine.—Corybulbine was first isolated by Freund and Josephi (Annalen, 1893, **277**, 1); *iso*corybulbine was found by Gadamer and Ziegenbein (Arch. Pharm. 1902, **240**, 634). They occur in corydalis roots in an amount of 0·05% (Gadamer, *ibid.* 24), and 0·185% respectively (Bruns, Arch. Pharm. 1903, **241**, 634). The yields vary considerably. Makoshi (Arch. Pharm. 1908, **246**, 381) isolated (I) from a Korean corydalis, possibly *C. ambigua* (*see also* Chou, A. 1929, 1085). Both alkaloids (I) and (II) are sensitive to light.

Corybulbine (V), $C_{21}H_{25}O_4N$, $[\alpha]_D$ +303·3°, m.p. 239–240°, crystallises from boiling $EtOH$ in colourless needles, sparingly soluble in $EtOH$, Et_2O, and $CH_3{\cdot}CO_2Et$, soluble in $CHCl_3$, acetone, or hot benzene. (V) is a weak base.

$B{\cdot}HCl$, colourless prisms, m.p. 245–250°, slightly soluble in H_2O; platinichloride and aurichloride are amorphous. By oxidation with iodine optically inactive dehydrocorybulbine, $C_{21}H_{21}O_4N$ (dark violet needles, from H_2O, m.p. 175–178°), is formed.

By reduction an optically inactive *r*-corybulbine is obtained, m.p. 220–222°, which has not been resolved with bromocamphorsulphonic acid (Bruns, Arch. Pharm. 1903, **241**, 650).

***iso*Corybulbine** (VI), $C_{21}H_{25}O_4N$, $[\alpha]_D$ +299·8°, m.p. 179–180°, crystallises from $EtOH$ in colourless leaflets more soluble in $EtOH$ than (V); by this property (VI) may be separated from (V). (IV) is a tertiary base with 1 OH and 3 OMe-groups. For colour reactions of (I) and (II), *see* Gadamer (*ibid.* 1902, **240**, 52). (II) is oxidised with iodine to dehydro*iso*corybulbine, which yields rac. *iso*corybulbine, m.p. 165–167° on reduction. Dobbie, Lauder and Paliatseas methylated the phenolic OH-group in (V) and obtained *corydaline* (J.C.S. 1901, **79**, 87), also (VI) on methylation yields corydaline (Späth and Dobrowski, Ber. 1925, **58**, [B], 1274). All 3 alkaloids give the same *apo*corydaline (hydrochloride, m.p. 220–222°) on demethylation (Bruns, *l.c.*). This shows that (V) and (VI) are closely related to corydaline which is a methyl ether of (V) or (VI). Späth and Dobrowski (*l.c.*) succeeded in demonstrating the exact positions of the phenolic groups and both alkaloids were finally obtained by partial demethylation of corydaline (Späth and Holter, Ber. 1926, **59**, [B], 2800), (V) having the phenolic OH-group in position 3 and (VI) in position 2 (*cf.* structure of corydaline).

d-*Tetrahydropalmatine* was isolated by Späth, Mosettig, and Tröthandl (Ber. 1923, **56**, 877) from *C. cava* grown near Vienna. The yield from dried corydalis roots is about 0·4%, the extraction was effected by the method of Gadamer (Arch. Pharm. 1902, **240**, 21). Separation of phenolic from non-phenolic bases was achieved by using caustic soda ; *d*-tetrahydropalmatine was separated from corydaline by the insolubility of its hydrochloride.

Tetrahydropalmatine (VII), $C_{21}H_{25}O_4N$, $[\alpha]_D^{17}$ +292·5° (in EtOH), m.p. 142°, crystallises from dilute EtOH, is easily soluble in organic solvents, except Et_2O and light petroleum. On exposure to air it is coloured yellow; by oxidation with iodine, the quaternary iodide of palmatine (m.p. 238–239°) is obtained. Späth and Mosettig (Ber. 1926, **59**, [B], 1496) synthesised *d*-tetrahydropalmatine starting from *d*-tetrahydroberberine (*q.v.*), removing the methylenedioxy-group with phloroglucinol-sulphuric acid and methylating the phenolic base. The product obtained was identical in every respect with natural (VII).

For constitution of (VII), *cf.* palmatine (CALUMBA ALKALOIDS).

Corypalmine (VIII), $C_{20}H_{23}O_4N$, m.p. 235–236°, $[\alpha]_D^{16}$ +280° (in $CHCl_3$), was first isolated by Späth, Mosettig, and Tröthandl (Ber. 1923, **56**, [B], 875) in a yield of about 0·005%. It forms small white crystals and is sparingly soluble in MeOH. By methylation of the 1 phenolic OH-group with diazomethane, *d*-tetrahydropalmatine (*q.v.*) is obtained. In a later paper (Ber. 1925, **58**, [B], 2133) Späth and Mosettig demonstrated the exact position of the OH-group in (VIII) and proved it to be *d*-tetrahydro-jatrorrhizine (*q.v.* calumba alkaloids). (VIII) was synthesised by Späth and Mosettig (Ber. 1927, **60**, [B], 383) from *d*-tetrahydroberberine, the methylenedioxy-group was replaced by OH groups with phloroglucinol-H_2SO_4 and the resulting phenolic base was partially methylated; from the mixture of products thus obtained, (VIII) could be isolated. The phenolic OH-group takes the same position 3 as in corybulbine (*q.v.*).

There is evidence for the existence of *iso*corypalmine in *C. cava*, differing from corypalmine by the attachment of the phenolic OH-group to C-atom 2 (*d*-tetrahydrocolumbamin), *cf.* Gadamer, Späth and Mosettig (Arch. Pharm. 1927, **265**, 675).

Group II.—CORYCAVINE SUB-GROUP.—This group comprises the three alkaloids corycavine (I), corycavamine (II), and corycavidine (III).

(I) was first isolated by Freund and Josephi (Annalen, 1893, **277**, 1), (II) by Gadamer, Ziegenbein, and Wagner (Arch. Pharm. 1902 **240**, 19), and (III) by Gadamer (Arch. Pharm. 1911, **249**, 30). (I) and (II) have both the same structure, (I) is the racemic form, (II) is optically active and is easily transformed into (I) by heating to above the melting-point (*see* F. von Bruchhausen, Arch. Pharm. 1925, **263**, 601).

Corycavine (I), $C_{21}H_{21}O_5N$; *cf.* Gadamer and von Bruchhausen (Arch. Pharm. 1922, **260**, 97) where earlier references are given ; it occurs in *C. cava* in amounts from 0·07% (Legerlotz, Arch. Pharm. 1918, **256**, 161) to 0·11% (Gadamer and von Bruchhausen, *ibid.* 161). (I) crystallises from EtOH or Et_2O in rhombic tablets, m.p. 216–218°, insoluble in cold EtOH and H_2O. B·HCl needles (from H_2O), m.p. 219° ; B·HBr quadrangular flat plates from H_2O ; B·methiodide rhombic tablets, m.p. 218°.

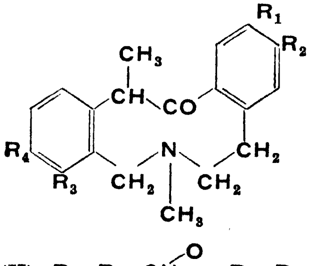
Resolution of (I) into *d*- and *l*- (II) has not yet been effected.

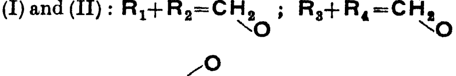
Corycavamine (II) occurs in an amount of 0·3% (Gadamer, Arch. Pharm. 1902, **240**, 84). It crystallises in rhombic columns from ether, alcohol, or $CH_3{\cdot}CO_2Et$, m.p. 148–149°, $[\alpha]_D$ +166° (in $CHCl_3$), transformation (II) → (I), *see above.* The salts except the sulphate crystallise very easily, the nitrate is sparingly soluble and is used to purify (II) ; B·HCl, small needles, soluble in H_2O ; B·HBr sparingly soluble needles ; B·HI, yellow voluminous, sparingly soluble needles.

Corycavidine (III), $C_{22}H_{25}O_5N$, occurs in an amount of 0·05%, $[\alpha]_D$ +203·1° (in $CHCl_3$), m.p. 212–213°, crystallises from $CHCl_3$–EtOH in transient, colourless crystals with 1 mol. of $CHCl_3$, practically insoluble in EtOH and Et_2O. Crystalline hydrochloride and sparingly soluble nitrate. By continued heating at 209° (III) is transformed into an optically inactive form, melting at 193–195°.

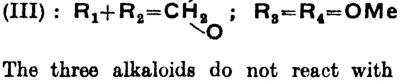
Pseudocorycavine (*see* Gaebel, Arch. Pharm. 1910, **248**, 249) is a mixture of (I) and (III) (*cf.* Gadamer, Arch. Pharm. 1911, **249**, 231) which is difficult to separate, but it can be effected by recrystallisation of the hydrochlorides.

Subject to a slight modification of (I) by Späth and Holter (Ber. 1927, **60**, [B], 1891), the constitutions of (I), (II), and (III) have been conclusively proved by F. von Bruchhausen (Arch. Pharm. 1925, **263**, 570).





$$\text{(I) and (II)}: R_1+R_2=CH_2\langle{}^{O}_{O}\ ;\ R_3+R_4=CH_2\langle{}^{O}_{O}$$



$$\text{(III)}: R_1+R_2=CH_2\langle{}^{O}_{O}\ ;\ R_3=R_4=OMe$$

The three alkaloids do not react with keto-reagents.

Pharmacologically the three alkaloids are of little importance (*cf.* Gadamer, Arch. Pharm. 1905, **243**, 147).

Group III.—Corytuberine Sub-Group.—Besides bulbocapnine (*q.v.*) this group comprises the closely related phenolic aporphine alkaloids *corytuberine* (I), *corydine* (II), and iso*corydine* (III). (I) and (II) occur in *C. cava* (0·7–1·5% and 0·3% respectively). (III) and the lävo- form of (II) were found in a Korean corydalis by Go (Amer. Chem. Abstr. 1930, **24**, 620); (II) and (III) have been isolated from *Dicentra canadensis* and *D. oregana* (Manske, Canad. J. Res. 1932, **7**, 258; 1934, **10**, 765). *Dicentra formosa* contains 0·02% of (I) and 0·03% of (II) (Manske, Canad. J. Res. 1934, **10**, 521).

For preparation of (I), *cf.* Gadamer, Arch. Pharm. 1911, **249**, 645; for preparation of (II), Arch. Pharm. 1902, **240**, 96.

Corytuberine (I), $C_{19}H_{21}O_4N,5H_2O$, $[\alpha]_D^{20}$ +282·6° (in EtOH), m.p. 240°, crystallises from hot H_2O in silky needles, soluble in EtOH slightly soluble in $CHCl_3$ and $CH_3·CO_2Et$, insoluble in benzene and Et_2O. The salts are crystalline but somewhat difficult to prepare, because (I) is a weak base and probably forms a phenolbetaine (Gadamer); the hydrochloride is sparingly soluble in H_2O.

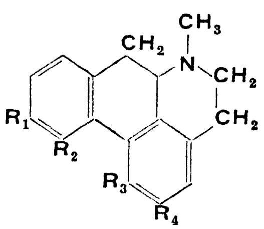
(II) and (III) are obtained by methylation of (I) with diazomethane; Gadamer experienced great difficulties in completely methylating (I); he only succeeded by doing it with diazomethane *in statu nascendi* in amyl ether solution (*l.c.* 1911).

Corydine (II), $C_{20}H_{23}O_4N$, $[\alpha]_D$ +204·4° (in $CHCl_3$), m.p. 124–125° from dilute EtOH with ½ mol. of EtOH or m.p. 149–150° (dry). It is readily soluble in $CHCl_3$ and EtOH, soluble in Et_2O. *Methiodide*, m.p. 190–191° (228–230° according to Manske, *l.c.* 1932), $[\alpha]_D^{20}$ +154·6°, easily soluble in H_2O. By iodine (II) is oxidised to the quaternary dehydrocorydine iodide (m.p. 248°); subsequent reduction yields racemic corydine, m.p. 168°, which can be resolved with tartaric acid into *d*- and *l*-forms (*l*-corydine, m.p. 151°, $[\alpha]_D^{26}$ −206°).

(II)·HCl, m.p. 258°, is sparingly soluble in H_2O; separation from the hydrochloride of (III) is thus possible.

***iso*Corydine** (III), $C_{20}H_{23}O_4N$, $[\alpha]_D$ +195·3° (in $CHCl_3$), m.p. 185°, crystallises in 4-sided tablets from $CH_3·CO_2Et$-MeOH. (III) is less soluble in Et_2O than (II); (III)·HCl is more soluble in H_2O than (II)·HCl. *Methiodide*, m.p. 213–214° (decomp.), $[\alpha]_D^{20}$ +143·3°, sparingly soluble in H_2O. No crystalline product was obtained by oxidation with iodine solution. For differences in colour reactions *cf.* Gadamer (*l.c.* 1911, 676).

Gadamer (*l.c.* 1911, 641, 669) on the basis of his investigations assigned structures to (I), (II), and (III) which had to be modified later in minor details. By synthesis of (I)-dimethylether (Gulland and Haworth, J.C.S. 1928, 1834, and Späth and Hromotka, Ber. 1928, **61**, [B], 1692) it was demonstrated that (I) belonged to the aporphine alkaloids. Späth and Berger (Ber. 1931, **64**, [B], 2038) synthesised corydine starting from bulbocapnine (*q.v.*) and conclusively demonstrated the arrangement of the OH and MeO groups in (I) and (III).



(I) : R_1 and R_4=MeO ; R_2 and R_3=OH.
(II) : R_1, R_2 and R_4=MeO ; R_3=OH.
(III) : R_1, R_3 and R_4=MeO ; R_2=OH.

Recently Isolated Corydalis Alkaloids —(*a*) *Non-phenolic bases.*—From *C. cava* grown near Vienna, Späth and Julian (Ber. 1931, **64**, [B], 1131) isolated *d-tetrahydrocoptisine*, $[\alpha]_D^{15}$ +310°, m.p. 203–204° (for constitution, *see* Coptisine), *d-canadine*, $[\alpha]_D^{15}$ +299°, m.p. 131–132° (for constitution, *see* Berberine) and *hydrohydrastinine*, m.p. 66°.

(*b*) *Phenolic Bases.*—Gadamer, Späth and Mosettig (Arch. Pharm. 1927, **265**, 675) isolated the 2 alkaloids: *d-tetrahydrocolumbamine*, m.p. 240–241° (for constitution, *see* Columbamine) and 2-9-*dihydroxy*-3-10-*dimethoxytetrahydroprotoberberine* (for numbering, *cf.* General Introduction to this article), m.p. 195°, which on complete methylation with diazomethane yielded *d*-tetrahydropalmatine. For new bases isolated from *Corydalis ambigua*, *see* Huang-Milnon (Ber. 1936, **69**, [B], 1757).

Schl.

CORYDINE *v.* Corydalis Alkaloids, Corytuberine Sub-Group.

CORYNANTHINE, one of the Yohimboa alkaloids.

CORYPALMINE *v.* Corydalis Alkaloids, Corydaline Sub-Group.

CORYTUBERINE *v.* Corydalis Alkaloids, Corytuberine Sub-Group.

COSTENES. The sesquiterpene hydrocarbons, *a*- and *β-costenes*, $C_{15}H_{24}$, were isolated by Semmler and Feldstein (Ber. 1914, **47**, 2692) from the roots of *Saussurea Lappa*. These hydrocarbons, the homogeniety of which is doubtful, have the following constants: *a*-, b.p. 122–126°/12 mm., d^{21} 0·9014, n_D^{21} 1·49807, $[\alpha]_D$ −12°; *β*-, b.p. 144–149°/18 mm., d_{22} 0·8728, n_D^{22} 1·4905, $[\alpha]_D$ +6°. No crystalline derivatives have been prepared.

J. L. S.

COSTOL. The primary sesquiterpene alcohol, *costol*, $C_{15}H_{24}O$, b.p. 169–171°/11 mm., d^{21} 0·9803, n_D 1·5200, $[\alpha]_D$ +13°, was separated by Semmler and Feldstein (Ber. 1914, **47**, 2687) from the oil from the roots of *Saussurea lappa*. The alcohol, which is probably dicyclic, gives on oxidation with chromic acid an *aldehyde*, $C_{15}H_{22}O$, b.p. 164–165°/15 mm., d^{22} 0·9541, n_D 1·50645, $[\alpha]_D$ +24°, *semicarbazone*, m.p. 217–218°.

J. L. S.

COSTUS, ESSENTIAL OIL OF. The oil distilled from the root of *Saussurea lappa* Clarke (*Aplotaxis lappa* Decaisne) indigenous to the mountain slopes of the Kashmir valley. The root is used for incense and to preserve the celebrated Kashmir shawls from the attack of moths. The oil is used in perfumery. Yield 1–3%.

Constituents.—Costic acid, costolactone, dihydrocostolactone, the sesquiterpene alcohol, costol (*q.v.*), a hydrocarbon aplotaxene and the two sesquiterpenes—*a*-costene and *β*-costene (*q.v.*), with traces of phellandrene and camphene.

Characters.—A light yellow oil, sp.gr. 0·982–0·987, optical rotation about +15°, n_D^{21} 1·510–1·520.

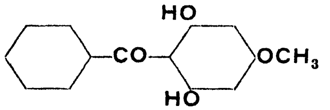
C. T. B.

COTARNINE, an oxidation product of narcotine, an opium alkaloid.

COTO BARK. True coto bark is obtained from Bolivia, the Amazons (Brazil), and Venezuela. It has been considered identical with Winter's bark [from *Drimys Winteri* Forst.], but its source is really unknown (Hesse, Annalen, 1894, **282**, 191). It comes into the market in long strips about 8 cm. broad and 12 mm. thick, and is tough and hard. The colour is cinnamon brown, and a cross-section shows numerous yellow spots. It has an aromatic odour, and contains *cotoin*, *dicotoin*, *hydrocotoin*, and *methylhydrocotoin*, resins, tannin, etc. The supply of the true coto bark is limited, and inferior barks, chiefly *para-coto bark*, are sold; these contain *protocotoin* and *methylprotocotoin*, but little or no cotoin.

Cotoin can be isolated from true coto bark by extracting the powdered bark with ether, removing the ether, and mixing the residue, whilst still hot, with light petroleum. A resinous oily mass separates from which the solution of cotoin is decanted. Cotoin forms yellow prisms, m.p. 130–131°, is difficultly soluble in cold water, readily soluble in hot, is fairly soluble in alcohol, ether and chloroform, but sparingly soluble in light petroleum or benzene. It dissolves in alkalis forming yellow solutions from which it is precipitated on acidification, it yields phloroglucinol and benzoic acid as decomposition products.

Cotoin has been the subject of much investigation, by Ciamician and Silber (Ber. 1891, **24**, 299, 2977; 1892, **25**, 1119; 1893, **26**, 777; 1894, **27**, 409, 841; 1895, **28**, 1549), Jobst N. Repert. Pharm. 1876, xxv, 23; Ber., 1878, **11**, 1031), Jobst and Hesse (Ber. 1877, **10**, 249; Annalen, 1879, **199**, 17), and Hesse (*l.c.*; Ber. 1893, **26**, 2790; 1894, **27**, 1182). As a result it has been shown to be 2:6-dihydroxy-4-methoxybenzophenone.



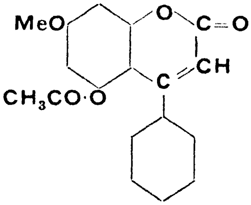
Späth and Fuchs (Monatsh., 1921, **42**, 267) obtained cotoin, hydrocotoin (cotoin methyl ether), and a small amount of cotoin dimethyl ether by methylating 2:4:6-trihydroxybenzophenone with less than one molecular proportion of diazomethane at −12°. The synthesis, however, does not establish the orientation of the methoxyl group in cotoin.

From a consideration of the products obtained by methylation and ethylation of cotoin, Späth and Wessely (Monatsh. 1928, **49**, 229) conclude that the methoxyl group of cotoin is in the *para*-position. The properties of the derivatives of cotoin obtained by *p*-toluenesulphonylation (Karrer and Lichtenstein, Helv. Chim. Acta, 1928, **11**, 789) also point to the same conclusion.

Cotoin has been used pharmaceutically in cases of diarrhœa and of phthisis.

The following derivatives of cotoin have been prepared:

Diacetylcotion, prisms, m.p. 94°, is produced by the action of acetic anhydride. If sodium acetate is used in the acetylation, the diacetyl derivative is accompanied by *methoxyhydroxyphenylcoumarin acetate*, m.p. 142°:



(Jobst and Hesse, Annalen, 1879, **199**, 28; Ciamician and Silber, Ber. 1894, **27**, 419).

Benzoylcotoin, prisms, m.p. 110–112°, and *dibenzoylcotoin*, needles, m.p. 134–135° (Hesse, Annalen, 1894, **282**, 194).

Dimethylcotoin, m.p. 138°, obtained by the action of methyl iodide and alkali on cotoin, yields a *monoacetyl* derivative, colourless needles, m.p. 150°, and hence probably has the formula:

$$HO{\cdot}C_6H{\cdot}Me(OMe)_2{\cdot}CO{\cdot}C_6H_5$$

(Ciamician and Silber, Ber. 1894, **27**, 418).

Dibromocotion, colourless needles, m.p. 116°, *cotoin oxime*, $C_{14}H_{13}NO_4$, plates, soluble in alcohol, difficultly soluble in water (Ciamician and Silber, Ber. 1894, **27**, 415).

Mononitrosocotoin, dark red leaflets or orange-yellow needles, m.p. 153–154° (Pollak, Monatsh. 1901, **22**, 996).

*Cotoinazo-*o*-toluene*, orange-yellow needles, m.p. 203–204°, *cotoinazo-*p*-toluene*, orange-yellow needles, m.p. 207–208°, and *cotoinazobenzene*, orange-yellow needles, m.p. 183–184°, *diacetylcotoinazobenzene*, scarlet needles, m.p. 155–156° (Perkin and Martin, J.C.S. 1897, **71**, 1149).

Cotoin ethyl ether (2-hydroxy-4-methoxy-6-ethoxybenzophenone), m.p. 91–92°, *cotoin methyl ethyl ether* (2:4-dimethoxy-6-ethoxybenzophenone), m.p. 103–104°, *cotoin diethyl ether* (4-methoxy-2:6-diethoxybenzophenone), m.p. 82–83°, b.p. 160–170°/0·001 mm. (Späth and Wessely, *l.c.*).

p-*Toluenesulphonylcotoin* (2-hydroxy-4-methoxy-6-*p*-toluene-sulphonyloxybenzophenone), m.p. 138°, *di-*p*-toluenesulphonyl* derivative, m.p. 144°. Methylation of the former gives the p-*toluenesulphonyl* derivative, m.p. 112°, of hydrocotoin (2-hydroxy-4:6-dimethoxybenzophenone) (Karrer and Lichtenstein, *l.c.*).

A number of polyhydroxybenzophenone derivatives, including products found in coto bark and related to cotoin, have been prepared by W. H. Perkin and Robinson (Proc. Chem. Soc. 1906, **22**, 305).

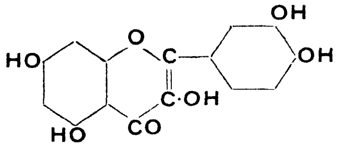
A. G. P. and E. J. C.

COTOIN *v.* Coto Bark.

COTTON FLOWERS. The flowers of the cotton plant, according to Watt (" Dictionary of the Economic Products of India "), are used as a dyestuff in the Manipur district.

The colouring matters present in the flowers of the ordinary Indian cotton plant, *Gossypium herbaceum*, have been studied by Perkin (J.C.S. 1899, **75**, 826 ; 1913, **103**, 650), who isolated a mixture of quercetin and gossypetin by digesting a concentrated alcoholic extract of the flowers with boiling dilute hydrochloric acid. The mixture was acetylated and the acetyl derivatives of the colouring matters separated by fractional crystallisation from acetic anhydride, in which acetylgossypetin is less soluble.

Quercitin, the aglucone of the glucoside *quercitrin*, the colouring matter of quercitron bark, is 3:5:7:3′:4′-pentahydroxyflavonol :



Gossypetin, $C_{15}H_{10}O_8$, yellow needles, m.p 311–313°, closely resembles quercetin in appearance, and is readily soluble in alcohol, but only very sparingly soluble in water. Concentrated alkaline solutions dissolve it forming orange-red liquids which, on agitation and dilution with water, become green, then blue, and finally assume a dull brown tint. Alcoholic lead acetate gives a deep red precipitate in the cold, passing into dull brown at the boiling-point, and with alcoholic ferric chloride a dull olive-green liquid is obtained.

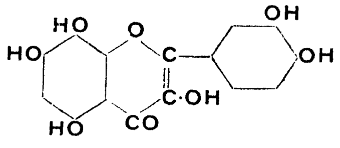
Gossypetin forms crystalline compounds with mineral acids and yields a *monopotassium* derivative, $C_{15}H_9O_8K$, with alcoholic potassium acetate. *Hexa-acetylgossypetin*, colourless needles, melts at 228–230°. By fusion with alkali, gossypetin gives protocatechuic acid and a phenolic substance which has not yet been identified.

When *gossypetin hexamethyl ether*, colourless needles, m.p. 170–172°, is hydrolysed with alcoholic potash, protocatechuic acid dimethyl ether and *gossypitol tetramethyl ether*, $C_{12}H_{16}O_6$, needles, m.p. 115–116°, are produced. In a similar manner, *gossypetin hexaethyl ether*, m.p. 144–146°, yields protocatechuic acid diethyl ether and *gossypitol tetraethyl ether*,

$$HO\cdot C_6H(OEt)_3\cdot CO\cdot CH_2\cdot OEt,$$

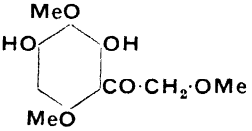
m.p. 110–111°. The latter forms an *oxime*, $C_{16}H_{25}O_6N$, m.p. 127–129°, and when oxidised with permanganate gives *gossypetonic acid*, $HO\cdot C_6H(OEt)_3\cdot CO\cdot COOH$, yellow needles, m.p. 154–155°.

As a result, Perkin concluded that gossypetin is hydroxyquercetin :

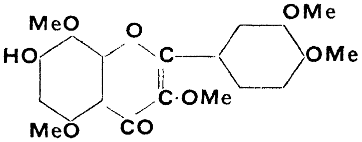


I.

By the oxidation of quercetin with chromic acid, Nierenstein and Wheldale (Ber. 1911, **44**, 3487) obtained quercetone, which, on simultaneous acetylation and reduction and subsequent saponification, yielded hydroxyquercetin. To this substance, which is not identical with gossypetin, formula (I) was assigned, and its synthesis was described by Nierenstein (J.C.S. 1917, **111**, 4). On the other hand, Baker, Nodzu and Robinson (*ibid.* 1929, 74) obtained results which confirm the work of Perkin but are irreconcilable with that of Nierenstein. These authors synthesised gossypetin by veratroylation of the trimethoxyresacetophenone (II). The hydroxypentamethoxyflavone (III) thus formed gave gossypetin (I) on demethylation.



II.



III.

Gossypitone.—When an alkaline solution of gossypetin is exposed to air, the blue liquid on acidification yields a reddish-brown precipitate which, on gentle warming, becomes crystalline. Again, if benzoquinone is added to a solution of gossypetin in cold absolute alcohol, a similar reaction occurs. On keeping for a few minutes crystals begin to separate, and by then heating to 50° a semi-solid mass is obtained. This substance, *gossypitone*, $C_{15}H_8OH$, consists of microscopic needles of a dull red colour, which are difficultly soluble in the usual solvents. It dissolves in dilute alkalis with a pure blue coloration and its solution in concentrated sulphuric acid is dull brown. Sodium bisulphite solution reconverts it into gossypetin. Gossypitone possesses strong dyeing properties, and gives the following shades on mordanted woollen cloth :

Aluminium . . .	Orange-brown.
Chromium . . .	Dull brown.
Tin	Orange-red.
Iron	Deep olive.

These shades are identical with those given in these circumstances by gossypetin itself, and it is accordingly evident that during the dyeing operation oxidation of the latter to gossypitone takes place.

The glucosides present in cotton flowers have been examined by Perkin (J.C.S. 1909, **95**, 2181), who in the first place employed the Egyptian variety. The Egyptian cottons appear, according to the researches of Messrs. Fletcher and Balls, to be derived from natural crosses of brown Peruvian cottons with the Sea Island variety.

Three glucosides, *quercimeritrin*, *gossypitrin*, and iso*quercitrin* were isolated, with difficulty, from a concentrated alcoholic extract of the flowers.

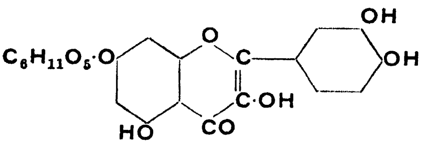
Quercimeritrin, $C_{21}H_{20}O_{12},3H_2O$, small, glistening, bright yellow plates, m.p. 247–249°, is insoluble in cold and fairly readily soluble in boiling water. Its alkaline solutions possess a deep yellow tint ; with aqueous lead acetate it gives a bright red precipitate, and with ferric chloride an olive-green coloration. *Octa-acetylquercimeritrin* forms needles, m.p. 214–216°. By hydrolysis with dilute sulphuric acid quercimeritrin yields quercetin and glucose.

On mordanted woollen cloth, quercimeritrin gives the following shades :

Aluminium . . .	Orange-yellow.
Chromium . . .	Reddish-brown.
Tin	Bright orange.
Iron	Olive-brown.

With the exception of the iron mordanted pattern, which is of a rather browner character, the colours thus produced closely resemble those given by quercetin itself when dyed in a similar manner, and are widely different from those given by rutin and quercitrin.

The position of the sugar group in quercimeritrin has been determined by Attree and Perkin (J.C.S. 1927, 234). With diazomethane the glucoside yields almost colourless needles of the *pentamethyl ether*, $C_{21}H_{15}O_7(OMe)_5,2H_2O$, m.p. 203–205°, sintering at 197°. By hydrolysis, colourless needles of a sparingly soluble *quercetin tetramethyl ether*, m.p. 284–285°, are obtained, the *acetyl* derivative of which melts at 174–176°. As this, when digested with alcoholic potash at 180°, readily gives veratric acid and phloroglucinol monomethyl ether, it is evidently the hitherto unknown 3:5:3′:4′-tetramethoxy-compound. Quercimeritrin, therefore, has the formula :



which is in harmony with its dyeing properties.

Quercimeritrin is also present in the flowers of the *Prunus emarginata* ? (Finnemore, Pharm. J. 1910, (iv), **31**, 604) and *Helianthus annuus* (Sando, J. Biol. Chem. 1926, **68**, 407).

Gossypitrin, $C_{21}H_{20}O_{13}$, yellow needles, m.p. 240–242°, $(+H_2O)$ m.p. 200–202°, dissolves in alkalis with a pale yellow coloration, and gives with lead acetate a deep red precipitate. It is almost insoluble in boiling acetone, a property which readily distinguishes it from quercimeritrin, which is fairly soluble in this solvent. When hydrolysed with dilute sulphuric acid, gossypitrin yields gossypetin and glucose. *Acetylgossypitrin*,

$$C_{21}H_{11}O_{13}(CO{\cdot}CH_3)_9,$$

colourless needles, m.p. 226–228°, is almost insoluble in alcohol.

Gossypitrin reacts, like gossypetin itself, with benzoquinone and forms a quinone, *gossypitrone*, $C_{21}H_{18}O_{13}$, maroon-coloured needles, which possess no definite melting-point although fusion of the product occurs about 255–259°. By the action of warm dilute sulphurous acid solution it is reconverted into gossypitrin.

Identical shades are given by gossypitrin and gossypitrone on mordanted wool :

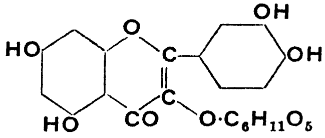
Aluminium . . .	Dull yellow.
Chromium . . .	Reddish-brown.
Tin	Bright orange.
Iron	Dark olive-brown.

and it is thus evident that the former is converted into the latter during the dyeing process.

The sugar residue of gossypitrin is probably attached to the hydroxyl group in the 7-position.

*iso***Quercitrin**, $C_{21}H_{20}O_{12},2H_2O$, pale yellow needles, m.p. 217–219°, is sparingly soluble in water and dissolves in alkaline solutions with a deep yellow tint. It gives a bright yellow precipitate with aqueous lead acetate and when hydrolysed yields quercetin and glucose.

By methylating *iso*quercitrin with diazomethane, Attree and Perkin (*l.c.*) obtained pale yellow, flat needles of a methylated derivative, m.p. 150–152°, which on hydrolysis gave 5:7:3′:4′-tetramethoxyflavonol. *iso*Quercitrin thus has the structure :



On mordanted wool *iso*quercitrin gives the following shades which are entirely distinct from those given by quercimeritrin and, although slightly paler, resemble those yielded by quercitrin :

Aluminium . . .	Golden-yellow.
Chromium . . .	Brownish-yellow.
Tin	Lemon-yellow.
Iron	Brownish-olive.

*iso*Quercitrin has also been isolated from brown-husked maize (Sando and Bartlett, J. Biol. Chem. 1922, **54**, 629) and from mulberry leaves (Oku, J. Agric. Chem. Soc. Japan, 1934, **10**, 1029).

Among the types of cotton flowers there are red, pink, yellow and white flowered plants. Perkin (J.C.S. 1916, **109**, 145) examined the following types : red flowered, *G. arboreum* Linn. ; pink, *G. sanguineum* Harsk ; yellow and white, two varieties of *G. neglectum* Tod, usually now treated as one species but originally described as *G. neglectum* and *G. rosarum*. As a result it was found that the red flowers of *G. arboreum* contain *iso*quercitrin, whereas in the yellow flowers of *G. neglectum*, gossypitrin and *iso*quercitrin were present. On the other hand, the white flowers of *G. neglectum* and the pink flowers of *G. sanguineum* gave amounts of colouring matter too small for complete identification, although the respective products obtained resembled in their properties apigenin and quercetin.

An examination of the ordinary Indian cotton flower, *G. herbaceum*, available only in small amount, showed the presence of gossypitrin and *iso*quercitrin. On the other hand, Neelakantam, Rao and Seshadri (Proc. Indian Acad. Sci. 1935, **2**, A, 490) find that the petals of *G. herbaceum* from Coimbatore, South India, contain gossypitrin, quercitrin (instead of *iso*quercitrin), and a flavonol glucoside *herbacitrin*, m.p. 247–249°, with small quantities of gossypetin. Herbacitrin forms an *octa-acetyl* derivative, m.p. 214–216°, and on hydrolysis yields *herbacetin*, m.p. 279–281°, identical with 3:5:7:8:4′-pentahydroxyflavone synthesised by Goldsworthy and Robinson (J.C.S. 1938, 56). The colour reactions of herbacitrin indicate that it is the 7-glucoside of herbacetin (Neelakantam and Seshadri, Proc. Indian Acad. Sci. 1937, **5**, A, 357).

According to Neelakantam, Rao and Seshadri (*ibid.* 1935, **1**, 887), quercetin and quercimeritrin are present in the flowers of *G. hirsutum* in proportions which vary with variety, locality and season. From the petals of *G. indicum*, Neelakantam and Seshadri (*ibid.* 1936, **4**, A, 54) isolated *gossypin*, m.p. 230° (decomp.), which by hydrolysis yielded gossypetin and glucose and a non-glycosidic *substance*, $C_{16}H_{12}O_7$, m.p. 255–257°, the *acetyl* derivative of which melts at 186–187°. In addition, gossypitrin, herbacitrin, and quercetin were isolated.

Gossypetin is also present in the flowers of the *Hibiscus sabdariffa* or " red sorrel " of the West Indies, a small shrub which is widely cultivated throughout the hotter parts of India and Ceylon (Perkin, J.C.S. 1909, **95**, 1855). The stems yield the " Rozelle hemp " of commerce.

A. G. P. and E. J. C.

COTTONSEED, COLOURING MATTER OF. Cottonseeds contain, in addition to cottonseed oil, a highly toxic phenolic substance, *gossypol*, which remains dissolved in the oil when this is expressed.

By extracting the oil with caustic soda and neutralising the extract, a voluminous precipitate of the colouring matter admixed with fatty acids and the products of its own oxidation separates. Marchlewski (J. pr. Chem. 1899, [ii], **60**, 84) isolated gossypol from a partially purified preparation of this character by extraction with ether and repeated crystallisation from acetic acid. The small yellow prisms melted at 188°, and dissolved in sulphuric acid with a cherry-red coloration, a reaction by which the presence of gossypol in cottonseed oil can be detected. Gossypol dissolves in alkalis forming yellow solutions which are readily susceptible to air oxidation and rapidly become violet and then slowly fade. An alcoholic solution of gossypol gives with ferric chloride a dark green coloration and with neutral and basic lead acetate a deep yellow precipitate. According to Marchlewski, gossypol appears to possess 2 hydroxyl groups, but contains no methoxyl groups, and is not a glucoside. It dyes iron-mordanted material a grey shade, and can be employed on cotton as a mordant for the basic colouring matters.

Carruth (J. Amer. Chem. Soc. 1918, **40**, 647) isolates gossypol from the decorticated cottonseed kernels which have been crushed by rollers before they are " cooked " in the oil mill. From these a considerable amount of oil is removed by percolation with light petroleum, and the residue is extracted with ether and the extract concentrated. The product is treated with acetic acid and, on keeping, crystals of *gossypol acetate* separate. To obtain gossypol itself, an ethereal solution of the acetate is treated with water and the ether distilled off. The gossypol thus remains suspended in the water as crystalline crusts.

A second interesting method consists in adding aniline to an ethereal extract of cottonseed. The solution, after warming on the water-bath and standing, gradually deposits an orange-yellow microcrystalline precipitate which apparently consists of an aniline salt of gossypol. The yield is practically quantitative, and the process may be used to estimate gossypol in extracts of cottonseed products. To regenerate gossypol, the aniline compound is dissolved in hot alcoholic potassium hydroxide, the aniline removed by steam distillation, and the gossypol precipitated by acidifying the alkaline liquid.

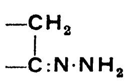
Gossypol has been examined by Clark (J. Biol. Chem. 1927, **75**, 725 ; 1928, **76**, 229 ; **77**, 81 **78**, 159 ; J. Amer. Chem. Soc. 1929, **51**, 1475, 1479), who isolated the substance by the method of Carruth (*l.c.*). After removal of acetic acid the product separated from a mixture of ether and light petroleum in crystalline form, m.p. 214° (decomp.). Analysis gave the formula $C_{30}H_{30}O_8$. Gossypol yields a *dioxime*, m.p. 315°, and by acetylation a *hexa-acetyl* derivative, m.p. 276–277°, four of the acetyl groups of which are readily hydrolysed, whilst the remaining two are more resistant to attack. Gossypol thus contains 2 carbonyl groups and 6 hydroxyl groups.

Gossypol acetate, $C_{30}H_{30}O_8{\cdot}C_2H_4O_2$, m.p. 189–190° (decomp.), a molecular compound of gossypol and acetic acid, is evidently the substance described by Marchlewski as the free colouring matter. It is a comparatively stable substance, and when heated does not evolve acetic acid readily below 180°. The absorption curve shows maxima at 3,780 Å and 2,390 Å and a minimum at 3,220 Å (Grünbaumówna and Marchlewski, Biochem. Z. 1936, **286**, 295).

When heated at 215°, gossypol loses 2 mols. of water and forms *anhydrogossypol*, m.p. 268° after softening at 229–230°.

With aniline, gossypol forms a *dianilide*, m.p. 302–303°, apparently a condensation product of 1 mol. of gossypol with 2 mols. of aniline and elimination of water, but not a salt of gossypol as Carruth (*l.c.*) has suggested.

According to Karrer and Tobler (Helv. Chim. Acta, 1932, **15**, 1204), gossypol, m.p. 199° yields a *quinoxaline* derivative, m.p. 298° (after sintering and decomposition), and is thus an α-diketone or, more probably, an *o*-quinone. The *dihydrazone* derivative, m.p. about 285°, gives with sodium ethoxide at 180° a *substance*, $C_{30}H_{34}O_6N_2$, which contains the grouping



$$\begin{array}{l}—CH_2\\ \;\;|\\ —C{:}N{\cdot}NH_2\end{array}$$

Two of the hydroxyl groups of gossypol titrate as acids, and two are resistant to hydrolysis when esterified.

Oxidation of gossypol with cold alkaline permanganate yields formic, acetic and *iso*butyric acids. The yield of the last-named is approximately one molecular proportion, and this is considered to indicate the presence of an *iso*butyl group in the side-chain of gossypol. With chromic acid, hexa-acetylgossypol gives a bright yellow substance, *tetra-acetylgossypolone*,

$$C_{25}H_{18}O_4(OAc)_4,$$

which chars at 230°. This reaction suggests the removal of C_5H_8 from, and the formation of two additional quinone groups in, the gossypol nucleus. (Clark, *l.c.*). With ozone, gossypol yields *gossypolic acid*, probably $(C_{12}H_{14}O_4)_2$, m.p. 241°, which is shown by colour reactions to be an α-hydroxy-acid. *Methyl methylgossypolate*, $[C_{12}H_{12}O_2(OMe)_2]_x$, m.p. 142°, gives *methylgossypolic acid*, m.p. 225°, by hydrolysis (Karrer and Tobler, *l.c.*).

Schmid and Margulies (Monatsh. 1935, **65**, 391), by catalytic reduction of gossypol, obtained *hydrogossypol*, $C_{30}H_{36}O_8$, decomposing at 320°, which does not form an additive compound with acetic acid but yields a *hexa-acetyl* derivative (decomp. 235°) on acetylation. When distilled with zinc dust it gives β-*iso*amylnaphthalene and a *substance* containing oxygen, m.p. 234–238°, b.p. 180°/12 mm. By oxidation of hydrogossypol with alkaline peroxide, butyric acid is obtained together with unidentified compounds.

By extracting cottonseeds with chloroform, Podolskaya (Biochem. Z. 1936, **284**, 401) isolated a red crystalline gossypol which differs from yellow gossypol in its absorption spectrum. On the other hand, both yield the same aniline derivative, and the red pigment changes to the yellow in alcoholic solution. It is suggested that the red colouring matter is present in the seed, and is changed to the yellow under the influence of reagents.

apoGossypol.—By heating gossypol with 40% sodium hydroxide at 100°, apo*gossypol*, $C_{28}H_{30}O_6$, is obtained together with formic acid resulting from the elimination of the 2 carbonyl groups originally present. *apo*Gossypol is considerably less toxic than gossypol. It yields a *hexamethyl ether*, m.p. 259°, and a *hexa-acetyl* derivative, m.p. 291°.

Oxidation of hexa-acetyl*apo*gossypol in acetic acid with chromic acid yields *tetra-acetyl*apo-*gossypolone*, $C_{22}H_{16}O_2(OAc)_4$, m.p. 230°. *apo*-Gossypol hexamethyl ether is oxidised in a similar manner to yellow *ψ-gossypolone tetramethyl ether*, $C_{28}H_{22}O_4(OMe)_4$, m.p. 210°. This change is considered to involve the formation of 4 quinone groups without loss of carbon from the *apo*gossypol skeleton.

B- and C-Gossypols.—When gossypol is heated to 186–190° it fuses with the evolution of vapour, and then solidifies to a black mass. On treating the residue with ether, a sparingly soluble yellow crystalline compound, *B-gossypol*, separates, which is much less toxic than gossypol and melts at about 246–248°. Again, by fusion with alkali, a second new crystalline substance, *C-gossypol*, can be obtained, and this, which is soluble in alkalis with a blue colour, is probably closely related to the purple oxidation product of gossypol referred to above.

D-Gossypol.—Cotton seed meal which has been submitted to the " cooking process " loses much of its toxic property, and then contains practically no gossypol. By extracting this product with aniline, the *aniline* compound of *D-gossypol* can be isolated (yield, 1·2%). Alcoholic potash converts this substance into *D-gossypol*, yellow crystals which darken and soften at about 256° (Carruth, *l.c.*).

Sherwood (J. Agric. Res. 1926, **32**, 793) observes that during the manufacture of cottonseed meals 75% or more of the gossypol present is converted into the less toxic *D*-gossypol, and this he suggests is a hydrolysis product of the unstable gossypol. According to Gallup (Ind. Eng. Chem. 1927, **20**, 59), the extent to which gossypol is converted into *D*-gossypol depends on temperature, time of heating, and amount of water present. Continued heating, especially in the presence of water, destroys the *D*-gossypol, finally giving a product free from both forms of gossypol and almost non-toxic.

According to Clark (*l.c.*), *D*-gossypol yields dianilinogossypol with aniline.

A. G. P. and E. J. C.

COTTONSEED OIL, an important by-product of the cotton industry is prepared on an enormous scale from the seeds of the several species of the cotton plant, *Gossypium* sp., which grows wild as a perennial shrub in the tropics, and is extensively cultivated (as an annual crop) for the sake of the fibre in hot but non-tropical regions in many parts of the world. In the United States the " Upland cotton," *G. hirsutum* L., in which the seed is covered with a short fuzzy down (" linters ") in addition to the longer cotton fibre, is cultivated, whereas in the Sea Islands and Egypt, *G. barbadense* is grown, which furnishes " naked " or " bald " seeds, from which all the cotton fibre (lint) can readily be stripped. The Indian and Asiatic varieties of cotton include the ill-defined species *G. herbaceum*, *G. arboreum*, *G. indicum* and *G. neglectum*, whilst the indigenous South American cotton plants are frequently classified as separate species *G. acuminatum* (=*G. peruvianum* Cav.) and *G. brasiliense* Macf. (=*G. peruvianum* Engl.). Whilst the native cottons yield almost naked seeds, fuzzy seeds from cultivated varieties of " Upland " cotton are also exported from Brazil.

For classification of the cottons, *see* Watt, " Wild and Cultivated Cotton Plants of the World," 1907 ; Kew Bull. 1926, No. 5, 193 ; 1927, No. 8, 321 ; J. B. Hutchinson, Mem. Cotton Res. Stat. Trinidad, Ser. A (Genetics), No. 12, 1935 ; T. H. Kearney and G. J. Harrison, J. Agric. Res. 1928, **37**, No. 8, 465 ; H. B. Brown, "Cotton," 1927 ; Angelasto, Boyle, Meloy and Stine, "The Cotton Situation," U.S. Dept. Agric. Year Book 1921, 323).

In this country,[1] cottonseed appears to have been first expressed in 1847, and refined edible cottonseed oil was being produced in France, from Egyptian seed, in the middle of the nineteenth century. In the United States, however, the development of the industry, hampered as it was by the lack of proper methods for decorticating the seed and for refining the oil, and further checked by the Civil War, was very slow ; prior to 1860 practically the whole of the seed not required for planting was wasted, and although numerous attempts at oil production were made from 1820 onwards, the commercial establishment of the cottonseed industry in America and its rapid progress may be said to date only from as late as 1867–1870. (For the early history of the cottonseed industry, *cf.* Lamborn, "Cotton Seed Products," New York, 1904.) Since then, and especially within the present century, the industry has expanded to such enormous dimensions that the United States, which formerly exported large quantities of cottonseed oil to Great Britain and Europe, now not only consumes internally the whole of her vast crop of over 3–4 million tons p.a. of seed (equivalent to about 510,000–700,000 tons of oil), but imports in addition a considerable amount of cottonseed oil (57,000 and 86,600 tons in 1936 and 1937 respectively) from the United Kingdom (from one-third to one-fifth of the total), Japan, Brazil and Egypt. The annual import of cottonseed into the United Kingdom (chiefly from Egypt, Sudan and British East Africa, and Brazil) amounts to some 600,000–700,000 tons, and the export of oil to some 23,000–40,000 tons. India, which was formerly an important supplier of seed to this country, has ceased to export seed since about 1932, the whole crop (*c.* 2,000,000 tons p.a.) being consumed locally and only the expressed cake being exported. Large quantities of cottonseed are also grown (chiefly for local use) in South Russia (*c.* 850,000 tons p.a. from 1931–1934) and China (*c.* 1,250,000 tons p.a.).

About 1,000 lb. of seed are obtained per bale (500 lb.) of cotton fibre produced. The seed consists of about 40–55% of shell ("hull") and 45–60% of kernel, and contains as a rule from 6 to 12% of water, 15 to 25% of oil, 19 to 24% of proteins, 24 to 31% of carbohydrates, 14 to 21% of crude fibre, and 3 to 4·5% of ash. The proportion of oil varies with the origin of the seed as well as with local climatic conditions ; thus on the average, whilst Egyptian seed contains up to 24% of oil and South American seed from 20 to 21%, East Indian seed averages about 18% and American seed about 19·5% of oil. For commercial statistics, the oil equivalent of cottonseed is taken as 17 or 18%.

A distinction must be made in practice between the "naked" or "bald" seed from Egypt, etc., which is processed in England, France, etc., and can be crushed and expressed directly, and the seed from the "fuzzy" varieties of cotton which need to be decorticated before expression, since, even after ginning and delinting, the seed-hulls retain a fuzzy coating of short fibres, the presence of which in the seed-cake would be undesirable. After removing as much as possible of this "linters" (which is used in the manufacture of guncotton, paper and other cellulose derivatives) in gin-like "delinting" machines, the seeds are passed through "hullers" in order to crack the hulls, which can then be separated from the kernels or "meats" by sifting through shaker screens. Chemical methods of removing the linters, *e.g.* by treatment with acid fumes (*see* Ardashev, Ind. Eng. Chem. 1933, **25**, 575 ; Ardashev and others, Cotton Ind. Trust, U.S.S.R., Coll. Papers, 1933, No. 1, 38, 40, 55, 83), are less frequently resorted to except for analytical purposes. The "meats," or in the case of the "bald" varieties the whole seeds, are then crushed and "cooked" (*i.e.* heated in the presence of open steam) before expressing the oil in hydraulic presses. Both the Anglo-American and the cage-type of press are commonly employed, but, of recent years, the continuous-acting expeller type of press has also been employed in the United States; such "expeller oil" is still frequently denoted by the misleading term "cold-pressed oil," although, in fact, the crushed seed is nowadays steamed and pre-heated before being passed into the expeller.

The extraction of the oil from the seed by means of solvents has also been proposed (*see* D. Wesson, Oil and Fat Ind. 1933, **10**, 151 ; de Raedt, Mat. Grasses, 1935, 10673).

Any "foots" or fragments of crushed seed-meal are separated or filtered off from the oil before storage for sale as "crude cottonseed oil." The separated "hulls" may be used as bedding for cattle, as a fertiliser, or as fuel ; according to Jamieson ("Vegetable Fats and Oils," A.C.S. Monograph, 1932 ; *cf.* Kress, Cotton Oil Press, 1930, **3**, No. 12, 33) increasing quantities, after removal of the "hull-fibre" (linters) in special machines, are ground to make "hull-bran," which is added to the expressed seed-cake intended for use as cattle-food. Proposals have also been made to work up the hulls by destructive distillation (*see* Randolph, Grove and Tucker, J. Elisha Mitchell Sci. Soc. 1932, **48**, 26) or for the recovery of pentosans, furfural, etc. (*see* Zakoshikov, Ivanova and Kurennova, Cotton Ind. Trust, U.S.S.R., Coll. Papers, 1933, No. 1, 87 ; Zukervanik and others, Bull. Univ. Asie Centr. 1935, No. 21, 69 ; Kao and Yü, J. Chem. Eng. China, 1936, **3**, 331).

Expressed cottonseed cake (or meal) serves as a valuable ingredient of cattle-food, whilst inferior grades are employed as fertiliser ; the use of cottonseed meal for human consumption has been suggested (*see* Wesson, Oil and Fat Ind. 1926, **3**, 121 ; Baumgarten, Cottonseed Oil Mag. 1924, **40**, No. 10, 28).

Standard methods for the analysis and evaluation of cottonseed, including determinations of oil, nitrogen, etc., have been published by the

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[1] As early as 1783–1789 a prize was offered by the Society of Arts of London for a satisfactory process for the preparation of oil and cattle-cake from cottonseed, but this was never claimed.

Amer. Oil Chem. Assoc. (Standard Methods of Analysis); U.S. Dept. Agric., Service and Reg. Announcements, Bur. Agr. Economics, No. 133, 1932; Assoc. of Off. Agric. Chem. (Official and Tentative Methods of Analysis); *see* Jamieson and McKinney, Oil and Fat Ind. 1930, **7**, 291; Meloy, *ibid.* 135; 1931, **8**, 187; for the determination of "lint" and "hull fibre," *see also* Freyer, Oil and Soap, 1935, **12**, 208, 259; McKinney and Jamieson, *ibid.* 1936, **13**, 139.

Raw cottonseed kernels are studded with cells containing a deep red-brown colouring matter, with which is associated a highly toxic phenolic substance "gossypol," $C_{30}H_{30}O_8$ (*see* COTTON SEED, Colouring Matter of).

Some of this toxic material, which occurs to the extent of about 0·4–1·2% of the kernel (*see* Schwartze and Alsberg, J. Agric. Res. 1923, **25**, 285; Gallup, Oil & Soap, 1936, **13**, 191), may pass into the oil, if this is really expressed in the cold; however, under the action of moist heat, incidental to the "cooking" process in commercial oil recovery, the gossypol appears to combine with the seed proteins and is converted into a harmless substance known as "bound gossypol" or "D-gossypol," so that the industrial press-cake, if properly prepared, should not possess any toxic properties (*see* Clark, J. Biol. Chem. 1928, **76**, 229; Oil and Fat Ind. 1928, (5), 237; 1929, **6**, No. 7, 15; Menaul, J. Agric. Res. 1923, **26**, 233; Oil and Fat Ind. 1928, **5**, 333. *N.B.*—The ill-effects occasionally observed to arise from the over-feeding of cattle on cottonseed meal, which were formerly attributed to the action of gossypol, are now considered to be, in large part at least, due to the lack of certain proteins and other dietary factors in the meal, and can be remedied by the addition of appropriate food supplements to the feed (*see* Clark, *l.c.*; Gallup and Reder, J. Agric. Res. 1935, **51**, 259; 1936, **52**, 65); for the determination of total and "bound" gossypol in cottonseed meal, *see* J. O. Halverson and Smith, Ind. Eng. Chem. [Anal]., 1933, **5**, 319; 1934, **6**, 356; 1937, **9**, 516.

Correspondingly, only traces of the order of 0·05% of gossypol (? "bound" gossypol) are to be found in commercial hot-pressed crude cottonseed oil *see* Royce, Oil and Soap, 1933, **10**, 183; 1934, **11**, 116); larger amounts (up to 1%) have been found in expeller-pressed and in solvent-extracted oils. However, any gossypol present in the crude oil is completely removed during the normal refining treatment with alkali.

Owing to the presence of the colouring matters (which include plant-pigments and resins, *see* Jamieson, Oil and Fat Ind. 1925, **2**, 101; Thornton, jun., *ibid.* 1934, **11**, 209), crude cottonseed oil has a ruby-red to almost black colour, the depth of the colour depending in the first instance upon the freshness of the seed. Seed that has been stored for a long period may undergo deterioration ("heating"), which is reflected in the inferior quality of the oil obtained therefrom. Crude cottonseed oil is valued and graded according to its flavour, acidity, refining loss, and the quality of the refined oil producible from it; in the American trade, 6 grades from "Prime" to "Low-Grade" in addition to "Extracted" and "Cold-Pressed" (*i.e.* expeller-) oils are recognised (*see* "Book of Rules" of the National Cottonseed Products Assoc.). Standard methods for the examination of crude cottonseed oils, including determination of "refining loss" and the behaviour in bleaching tests are issued by the above body; *cf. also* Official Methods of the Amer. Oil Chemists' Society. The usual determination of "refining loss" has been modified by McLeod (Oil and Soap, 1936, **13**, 67) in order to render it applicable to the examination of English pressed-oils.

The crude oil is refined by treatment with dilute caustic soda at a temperature not exceeding 120°F. (49°C.), whereby the free fatty acids are neutralised, and the soap formed ("soap-stock") falls to the bottom of the vessel, carrying with it the brown colouring matter and other impurities, so that the supernatant neutral oil is of a bright yellow colour. This oil, which is washed to remove traces of soap, is known as "summer yellow oil," and may be bleached with adsorbent earths and deodorised as required. Oils intended for technical purposes may be treated with chemical bleaching agents.

The best qualities of refined oil, which have not been bleached with chemicals, are consumed in enormous quantities for edible purposes; thus it is estimated (Jamieson) that of the total production of cottonseed oil in the United States, 16% is employed as a salad or cooking oil, 2% for margarine manufacture, and 70% (much of it after hardening by catalytic hydrogenation) in the manufacture of shortenings (lard substitutes); the balance of 12% of technical oil, and also the fatty acids recovered by working up the "soap-stock," are chiefly utilised in the manufacture of various types of soap and soap-powders. The Indian and Egyptian cottonseed oils are used to a greater extent in soap-making.

By the destructive distillation of cottonseed oil combustible gases and hydrocarbon oils can be produced (*see* Egloff, Ind. Eng. Chem. 1932, **24**, 1426; Martin, Bull. Mat. Grasses, 1932, **16**, 97), and it is possible that the application of such processing to low-grade crude oils, or to cottonseed itself, may have a certain commercial significance in remote districts, such as Central Africa, where imported petroleum products are abnormally expensive.

Refined cottonseed oil ("summer oil") is, at ordinary temperatures, a pale yellow oil of characteristic but not unpleasant flavour; on standing at about 12°C. a deposit of "stearin," *i.e.* higher melting glycerides, is formed. As this "stearin" would be objectionable in the case of oils intended for use as table or salad oils, it is removed on the large scale by chilling the oil to a low temperature (5° C. or lower) and filtering off the deposited glycerides; the filtered oil, known in commerce as "winter oil" ("demarganinated" or "destearinated" oil), is required to remain clear and bright when kept at a temperature of 0°C. for 5½ hours; the discarded "stearin" is used in the manufacture of shortenings. The specific gravity of refined summer cottonseed oil ranges from 0·923 to 0·925 at 15·5°C.; the saponification value varies from 190 to 196 and the iodine value from 103 to 115; about 1% of unsaponifiable matter is present. On the whole, the oil from Egyptian seed tends to have a lower density and iodine value than the North American product (*see* Jamieson and Baughman, J. Amer. Chem. Soc. 1920, **42**, 1197; Oil and Fat. Ind. 1926, **3**, 347; 1927, **4**, 131; Perdrigeat, J. Pharm. Chim. 1930, [viii], **12**, 307); thiocyanogen values of 63–64·8 are recorded for three Egyptian oils by Atkinson (Analyst, 1934, **59**, 399). Analyses of cottonseed oils by Jamieson and Baughman (*l.c.* 1927) and Hilditch (Hilditch and Rhead, J.S.C.I. 1932, **51**, 200T; Hilditch and Jones, *ibid.* 202) show that the fatty acids of cottonseed oil contain from 19 to 22% of palmitic acid, 24 to 34% of oleic acid, and 39 to 50% of linoleic acid; only from 1·5 to 2·5% of stearic acid is present together with small amounts (0·5–3%) of myristic acid (?) and arachidic acid ($<1\%$). Practically the whole of the palmitic acid is associated with unsaturated fatty acids in mixed glycerides, only about 1·5% of fully saturated glycerides being present; the balance of the oil appears to consist of about 60% of mono-palmito-glycerides, 15% of di-palmito-glycerides, and 24% of mixed triglycerides of oleic and linolic acids (Hilditch and Jones, J.S.C.I. 1934, **53**, 13T). S. Ueno and Iwai (J. Soc. Chem. Ind. Japan, 1935, **38**, Suppl. 602) report the following composition for the fatty acids in a sample of fully hydrogenated cottonseed oil: myristic acid, trace; palmitic acid, 17%; stearic acid, 76%; higher saturated acids (arachidic acid), 7%.

Besides the sterols (unsaponifiable matter, which includes β-sitosterol, stigmastanol and waxy matter, *see* E. S. Wallis and Chakravorty, J. Org. Chem. 1937, **2**, 335; Anderson and Moore, J. Amer. Chem. Soc. 1933, **45**, 1944), traces of plant pigments (flavone derivatives), and phospholipins are also present in the refined oil; these occur in greater amount in crude cottonseed oil, together with a number of other minor components—raffinose, pentosans, proteoses, peptones, phytosterolins, inosite phosphates, etc. (Jamieson and Baughman, J. Oil and Fat. Ind. 1924, **1**, 31; 1925, **2**, 101; 1926, **3**, 153, 347); a small but bulky precipitate (known as "settlings") which occasionally settles out from a filtered crude oil consists of a mixture of such adventitious "impurities."

Cottonseed oil typifies a semi-drying oil: in the Livache test it absorbs 5·9% of oxygen in 24 hours. By blowing air through cottonseed oil at a temperature of 90–100°C., oxygen is absorbed with the formation of a small amount of "oxidised acids," while the acetyl value, viscosity, and density rise considerably. This reaction can be applied on the large scale to the preparation of *blown cottonseed oil* which was formerly used to a considerable extent in admixture with mineral oil to form lubricating oils of the *marine oil* type.

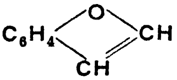
As stated above, hydrogenated (hardened) cottonseed oil is used to an enormous extent as an ingredient of shortenings.

For the identification of cottonseed oil, and for the detection of it in other oils and fats (down to 1% in favourable circumstances), the **Halphen colour test**[1] is most useful, this test is usually carried out as follows: 1–3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; 1–3 c.c. of a 1% solution of flowers of sulphur in carbon disulphide is added, and the test-tube is immersed in boiling water (or, better, boiling brine); the heating is continued for 2 hours or until a red coloration, indicating the presence of cottonseed oil, appears (usually within 20–30 minutes); the intensity of the colour depends in the first instance upon the proportion of cottonseed oil in the sample, but also varies somewhat with different specimens of this oil. The reagent which produces the colour appears to be an impurity in the amyl alcohol (Gastaldi), and the test may be rendered more delicate by replacing this solvent by pyridine; in this way, it is claimed that 0·25% of cottonseed oil may be detected (Gastaldi, Annali Chim. Appl. 1914, **2**, 203; Pieraerts and Simar, Mat. Grasses, 1928, 8222, 8312; *see* "German Standard Methods for the Analysis of Oils and Fats" (Wizoeff). According to Shelley (Analyst, 1925, **50**, 132; *see* Gastaldi, *l.c.*; "British Pharmacopœia," 1932) better results are obtained with the original Halphen reaction if the test-tube is sealed before heating. Although the Halphen test cannot be used for quantitative analysis, it must be considered, if positive, as one of the best means for the qualitative detection of cottonseed oil; a negative result, however, is no conclusive proof of the absence of this oil in a mixture, as the colour-producing constituent may be destroyed by heating or blowing the oil, or even by rancidification on prolonged storage; the test may also fail with hydrogenated cottonseed oils.

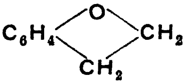
E. L.

COUCH GRASS. Associated in couch grass with triticin (a carbohydrate resembling inulin) are dextrose, mucilage, mannitol, and inositol) (*v.* AGROPYRUM).

COUMARANE. Coumarane, or hydrocoumarone, is prepared by reducing coumarone in alcoholic solution with sodium (Alexander, Ber. 1892, **25**, 2409). It forms a colourless oil, b.p. 188–189°, and gives in sulphuric acid by addition of ferric chloride a violet coloration.



Coumarone.



Coumarane.

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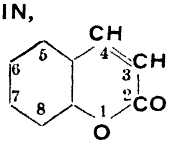
[1] Actually, this test is not specific for cottonseed oil, as the seed oils from most plants of the family Malvaceæ, and of certain allied families of the cohort Malvalæ (Bombacaceæ, Tiliaceæ, etc.) give positive reactions of greater or less intensity (*see* S. Ivanov, Ber. deut. pharm. Ges., 1927, **45**, 588; Pieraerts, Mat. Grasses, 1927, 7980). Of such oils, however, only kapok oil (which is not yet imported into America) is of any commercial importance. According to Melenbacher (Oil and Soap, 1936, **13**, 136) the presence of kapok oil may be detected by a characteristic turbidity which is formed when a chloroform solution containing kapok oil is treated with alcoholic silver nitrate. It may be noted, also, that the body-fat (*e.g.* lard) from animals which have been fed on cottonseed cake may give a weak positive Halphen reaction: in such a case, the suspected presence of cottonseed oil must be confirmed by the phytosteryl acetate test.

COUMARIN,



was obtained by Vogel (Gilb. Ann. 1820, **64**, 163) from the tonka bean, from melilot, and from woodruff but was mistaken for benzoic acid. It was first recognised as a distinct substance by Guibort, who gave it the name *coumarin*. It is a normal constituent of lavender oil and is very widely distributed in the plant kingdom (Gildemeister and Hoffman, " Die ätherischen Öle," 1928, Vol. I, p. 652). It occurs in plants as a glucoside which is hydrolysed by an enzyme present in the plant ; for its determination in plants, *see* Duncan and Dustman, Ind. Eng. Chem. [Anal.], 1934, **6**, 210.

It is prepared from tonka beans with 80% alcohol, followed by precipitation with water (Wöhler, Annalen, 1856, **98**, 66) ; it may also conveniently be extracted from melilot (Obermayer, Z. anal. Chem. 1913, **52**, 185).

It was first prepared synthetically by Perkin by heating the sodio-derivative of salicylaldehyde with acetic anhydride (J.C.S. 1868, **21**, 53) or, better, by boiling together salicylaldehyde, acetic anhydride and anhydrous sodium acetate (*idem., ibid.* 1887, **51**, 388 ; *see* Tiemann and Herzfeld, Ber. 1877, **10**, 284). Yanagisawa and Kondô (J. Pharm. Soc. Japan, 1921, 498) have described an improved method, using iodine as a catalyst, which is claimed to give a 70% yield. Perkin's method is that most frequently used for the technical production of coumarin. A variant of the process consists in the treatment of salicylaldehyde with acetic anhydride at 180° (Reychler, Bull. Soc. chim. 1897, [iii], **17**, 516).

Another method used commercially is the condensation of salicylaldehyde with malonic acid in acetic acid, followed by decarboxylation by heating the coumarin-3-carboxylic acid so formed (Stuart, J.C.S. 1886, **49**, 367).

Coumarin is also formed by heating a mixture of phenol and malic acid with sulphuric acid or zinc chloride (von Pechmann, Ber. 1883, **16**, 2119 ; 1884, **17**, 929, 1649) ; this may be extended to the synthesis of substituted coumarins, phenol homologues being employed (*see* Bailey and Boettner, Ind. Eng. Chem. 1921, **13**, 905). The most important method of obtaining substituted coumarins is by the condensation of phenols with ethyl acetoacetate or its alkyl derivatives in the presence of sulphuric acid; thus, phenol and ethyl acetoacetate yield 4-methylcoumarin (von Pechmann and Duisberg, Ber. 1883, **16**, 2127 ; von Pechmann and von Krafft, *ibid.* 1901, **34**, 421 ; Peters and Simonis, *ibid.* 1908, **41**, 831). Phenols containing alkyl, hydroxyl, or dialkylamino groups in the *m*- or 2:4- positions give good yields in the reaction, but condensation is prevented by the presence of nitro, carboxyl or carbethoxy groups (Clayton, J.C.S. 1908, **93**, 2018). Phosphoric acid is said to be superior to sulphuric acid as a catalyst for this reaction (Chakravarti, J. Indian Chem. Soc. 1931, **8**, 619 ; 1935, **12**, 536) while ethyl alcoholic hydrogen chloride brings about condensation in good yield when the ordinary method fails (Appel, J.C.S. 1935, 1031).

Coumarin forms rhombic crystals, m.p. 70°, b.p. 291°. It has a pleasant aromatic odour and is sparingly soluble in hot water, readily soluble in boiling water, and very soluble in alcohol and ether. Crude coumarin may be purified by repeated crystallisation from light petroleum (Claassen, Pharm. J. 1897, **4**, 161).

Hot concentrated alkalis convert coumarin into salts of coumaric acid (*cis-o*-hydroxycinnamic acid) from which coumarin is re-formed by heating with acetic anhydride. Reduction of coumarin with sodium amalgam in water or alcohol or with zinc and sodium hydroxide yields melilotic acid (Zwenger, Annalen Suppl. 1867, **5**, 122 ; 1872, **8**, 32 ; Fries and Fickewirth, Annalen, 1908, **362**, 30, 35). On nitration 6-nitrocoumarin is the principal product (Delalande, *ibid.* 1842, **45**, 337 ; Morgan and Micklethwait, J.C.S. 1904, **85**, 1233) together with a small amount of 8-nitrocoumarin (Dey and Krishnamurthi, J. Indian Chem. Soc. 1927, **4**, 197). Sulphonation yields, first, coumarin-6-sulphonic acid and then the 3:6-disulphonic acid (Perkin, J.C.S. 1871, **24**, 52 ; Sen and Chakravarti, J. Indian Chem. Soc. 1928, **5**, 433).

The mercuration of coumarins has been studied by a number of workers (Sen and Chakravarti, *ibid.* 1929, **6**, 847 ; Naik and Patel, J.C.S. 1934, 1043 ; Chakravarti, J. Indian Chem. Soc. 1935, **12**, 139) and the introduction of arsenic into the coumarin nucleus by Goswami and Das-Gupta (*ibid.* 1931, **8**, 417).

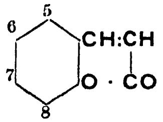
Sodium bisulphite reacts with coumarins to give *β*-sulphonic acids (Dodge, J. Amer. Chem. Soc. 1916, **38**, 448 ; 1930, **52**, 1724 ; Dey and Row, J.C.S. 1924, **125**, 554), a reaction that has successfully been applied for the determination of coumarin (Radcliffe and Sharples, Perf. and Essent. Oil Rec. 1924, **15**, 396, 437 ; 1925, **16**, 20 *et seq.*).

In Germany, woodruff is steeped in white wine, to which it imparts the pleasant aroma of coumarin (*Maiwein, Maitrank*). Instead of woodruff, an alcoholic solution of coumarin is employed for the same purpose (*see* Simonis, " Die Cumarine," 1916, p. 69). In large doses coumarin is said to have a narcotic action.

Coumarin has the agreeable odour of asperula and is used in perfumery for the preparation of asperula essence. It is also frequently used to adulterate vanilla extract. For its determination in vanilla essence, *see* Winton and Silverman, J. Amer. Chem. Soc. 1902, **24**, 1128 ; Winton and Bailey, *ibid.* 1905, **27**, 719.

H. N. R.

COUMARIN GLYCOSIDES. Coumarin



which has itself no free hydroxyl group, exists in glucoside form as *o*-coumaric acid glucoside, known as *melilotin,*

$$C_6H_{11}O_5\cdot O\cdot C_6H_4\cdot CH:CH\cdot CO_2H.$$

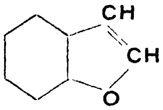
The aglucones of the hydroxy coumarin glucosides are :

Skimmin . . .	7-hydroxycoumarin.
Æsculin . . .	6:7-dihydroxycoumarin.
Cichorin . . .	6:7-dihydroxycoumarin.
Daphnin . . .	7:8-dihydroxycoumarin.
Scopolin . . .	6-methylæsculetin.
Fabiatrin . . .	6-methylæsculetin.
Fraxin . . .	6-methoxy-7:8-dihydroxycoumarin.

Skimmin has the glucose attached at position 7, as also has daphnin. In æsculin it is at position 6 (Head and Robertson, J.C.S. 1930, 2434), in cichorin at position 7 (Merz. Arch. Pharm. 1932, **270**, 476), and in fraxin at 8 (Wessely and Demmer, Ber. 1928, **61**, [B], 1279 ; 1929, **62**, [B], 120). Scopolin contains two glucose residues, fabiatrin only one.

E. F. A.

COUMARONE, 2:3-benzfuran,



occurs in the coal-tar fraction of b.p. 165–175°. After removing pyridine bases and phenols by treatment with acid and alkali, the oil is treated with bromine at 0°, and the dibromide thus obtained reduced to coumarone with alcoholic potash and sodium amalgam (Kraemer and Spilker, Ber. 1890, **23**, 78 ; Burda and Sukatscheva, Ukrain. Chem. J. 1931, **6**, [Sci.], 169). It may also be obtained from this source by adding picric acid to the oil, when coumarone picrate crystallises out. This is separated, decomposed with hot water or dilute alkali, and the coumarone obtained by steam distillation. The picric acid is recovered and used for another operation (G.P. 53792 ; B.P. 1422, 1890). It may be separated from accompanying indene by condensation of this with ethyl oxalate (Thiele, Ber. 1900, **33**, 3400).

It is obtained synthetically by heating *o*-hydroxy-ω-chlorostyrene with caustic potash (Komppa, Ber. 1893, **26**, 2971), by heating phenoxyacetaldehyde with zinc chloride in acetic acid (Stoermer, Annalen, 1900, **312**, 261), and by heating phenoxyacetaldehyde diethylacetal with anhydrous oxalic acid (Stoermer, *l.c.*).

Coumarone is a colourless oil of aromatic odour, b.p. 173–175°/760 mm., 62–63°/15 mm., $d_4^{22\cdot7}$ 1·0913, $n_D^{22\cdot7}$ 1·5645, and is insoluble in water but soluble in alcohol and ether. It may be characterised by means of its picrate, m.p. 102–103°, and 1:3:5-trinitrobenzene derivative, m.p. 104°. It is stable to alkalis, ammonia, potassium cyanide and hydrochloric acid but yields a series of polymers with sulphuric acid (*v.* COUMARONE RESINS). The coal-tar fraction, b.p. 185–195°, contains methylcoumarones (Stoermer and Boes, Ber. 1900, **33**, 3013).

H. N. R.

COUMARONE RESINS. Kraemer and Spilker (Ber. 1900, **33**, 2257 ; 1901, **34**, 1887) found that coumarone was polymerised by treatment with sulphuric acid ; Heusler (Z. angew. Chem. 1896, **9**, 318) found that aluminium chloride had a similar action, and Stein (*ibid.* 1919, **32**, 246) showed that stannic chloride was also an efficient catalyst for this polymerisation.

Technical coumarone resins are mixtures of coumarone and indene polymers obtained by treatment of coal-tar naphtha of b.p. 150–200° with suitable catalysts, notably sulphuric acid. Ellis and Rabinovitz (Ind. Eng. Chem. 1916, **8**, 797) made a thorough study of this process and concluded that sulphuric acid was the most effective catalyst ; ferric chloride or aluminium chloride (G.P. 446707) and fuller's earth mixed with ferric sulphate (U.S.P. 1894934) have also been claimed to be effective catalysts, while according to Bojanowski, Giziński and Rabek (Przemysł Chem. 1934, **18**, 321) almost colourless resins are obtained by using a mixture of sulphuric acid, acetic acid and water in the ratio 15 : 4 : 1. For discussions of the technical procedure, *see* Marcusson, Chem.-Ztg. 1919, **43**, 93, and Glaser, Brennstoff-Chem. 1921, **2**, 99, 113.

The best quality coumarone resins are pale amber solids melting above 130°. They are classified according to colour and hardness ; resins softening above 50° are termed " very hard," between 40° and 50° " hard," and between 30° and 40° " medium hard." For methods for their examination, *see* Marcusson, Chem.-Ztg. 1919, **43**, 109. Coumarone resins differ from many other resins in that they are neutral and unsaponifiable ; although somewhat unsaturated they are unaffected by most reagents ; on heating above 300° they undergo partial depolymerisation. Technically, they find wide application, being especially useful in the manufacture of varnishes, printing inks, waterproofing materials, rubber compositions and chewing gum. For a complete review of the chemistry and application of coumarone resins, *see* Ellis, " The Chemistry of Synthetic Resins," 1935, Vol. I, ch. 5–7.

H. N. R.

COVELLINE or COVELLITE. Native cupric sulphide, **CuS**, crystallising in the hexagonal system. Crystals are rare and have the form of thin six-sided plates. Fine large crystals have been found at Butte in Montana. The mineral has a characteristic indigo-blue colour, hence the name *indigo-copper* (Ger. *Kupferindigo*). It occurs in most copper-mines as a blue, earthy coating on other sulphide ores of copper, and is sometimes found in sufficient quantity to be of importance as an ore, *e.g.* at Butte in Montana, and Copiapo in Chile. Covellite containing platinum (as the mineral *sperrylite*, $PtAs_2$) is mined in the Medicine Bow Mountains in Wyoming.

L. J. S.

COW PEA or CHINA BEAN. The seed of the legume *Vigna sinensis* (L.) Endl. (or *Dolichos sinensis*, L.), are variously coloured, approximately ½ in. long, and are formed in long narrow pods often more than a foot in length. The peas are eaten as a vegetable, either green or dry, and the whole plant serves as a forage crop for cattle.

Analyses of the beans average :

	Edible green beans. %	U.S. Dept. Agric. (1906). %	Rhodesian Dept. Agric. (1934). %
Water . . .	66·0	14·8	13·9
Protein . .	9·4	20·8	23·4
Fat	0·6	1·4	1·8
N-free extract.	22·7	55·7	5·9
Fibre . . .	—	4·1	51·6
Ash	1·4	3·2	3·4

According to Osborne and Campbell (J. Amer. Chem. Soc. 1897, **19**, 494) the protein constituents of the cow pea include 3 globulins: (i) *Vignin*, the major constituent (C 52·6, N 17·3, S 0·5%) ; (ii) *phaseolin* (C 52·3, N 16·7, S 0·5%) ; and (iii) a soluble globulin (C 53·2, N 16·4, S 1·1%).

Osborne and Heyl (Amer. J. Physiol. 1908, **22**, 362) found the products of hydrolysis of *vignin* to be :

	%		%
Glycocoll. . .	0·00	Phenylalanine .	4·69
Alanine . . .	0·78	Proline . . .	4·41
Valine . . .	0·29	Tryptophan . .	+
Leucine . . .	6·73	Arginine . . .	6·04
Aspartic acid .	2·94	Lysine . . .	3·77
Glutamic acid .	12·84	Histidine. . .	2·71
Tyrosine . . .	2·03	Ammonia . .	2·18

Jones *et al.* (J. Biol. Chem. 1924, **62**, 183) show *vignin* to contain cystine 0·52% and tryptophan 1·65%.

Adolph and Chiang (Chinese J. Physiol. 1935, **9**, 347) separate five fractions among the proteins of cow pea, viz.

	%
Vignin (Globulin A)	45
Glutelin	25
Albumin	15
Globulin B	10
Globulin C	5

and record the high cystine content of the globulins and albumin and the high lysine content of the glutelin. Bhagvat (J. Indian Inst. Sci. 1935, **18**, A, 39, 137) also examined the proteins and confirms the high cystine content of the globulins.

Average analyses of the green parts of the cow pea as used for fodder are recorded by the U.S. Dept. of Agriculture as :

	Green fodder, %	Hay, %
Water	83·6	10·7
Protein	2·4	16·6
Fat	0·4	2·9
N-free extract	7·1	42·2
Fibre	4·8	20·1
Ash	1·7	7·5

A. G. Po.

" CRAB'S EYE " *v.* ABRUS PRECATORIUS.

CRANBERRY. The fruit of the American bog plant *Vaccinium macrocarpon* Ait. A smaller species (*V. Oxycoccus*, L.) occurs both in Europe and America. A related species (*V. vitio-idæa*) is known as the mountain or red cranberry, red whortleberry or cowberry in England, and as foxberry in the United States. The fruits are notable in keeping for a long time without decomposition, largely because they contain appreciable amounts of benzoic acid. The extremely sour fruit find widespread use in the form of jam or jelly.

Average analyses of cranberries are :

	American. %	European. %
Water	87·8–88·8	89·3–89·6
Protein . . .	0·35–0·5	0·10–0·12
Fat	0·57–0·97	—
N-free extract .	9·0–10·1	10·1
Free acids [1] . .	2·3–2·4	2·3
Sugars . . .	3·5–4·1	1·5
Fibre	1·1–1·5	—
Ash	0·15–0·18	0·15–0·17

[1] Calculated as citric acid.

Cranberry juice contains invert sugar 87·1, acids (calculated as malic acid) 19·0, ash 3·0, nitrogen 0·11 g. per litre, and either because of the benzoic acid content or because of the small amount of nitrogen present is not fermentable by yeast.

While all investigators agree on the presence of benzoic acids (0·02–0·09%) in cranberries, there seems some difference of opinion as to the nature and proportion of other acids occurring in the fruit. Citric and malic acids are generally reported in American cranberries ; Stolle (Z. Ver. deut. Zucker-Ind. 1900, **37**, 609) found glyoxylic acid in European fruit, and Rising (Kgl. Landtbruks. Akad. handl. Tidskr. 1914, 329) also found *iso*valeric acid. According to Isham *et al.* (Massachusetts Agric. Exp. Sta. Bull. 1935, No. 315) malic acid is present in mature and immature fruit in similar proportions (0·26%), whereas the citric acid content declines somewhat (1·31–1·07) with advancing maturity. The same authors also record more than 0·5% of quinic acid in the fruit.

Rising (*l.c.*) also isolated from cranberries the glucoside *vacciniin*,

$$C_6H_{11}O_6{\cdot}COC_6H_5.$$

The ash of American cranberries contains: K_2O 48·0, Na_2O 6·6, CaO 18·6, MgO 6·8, Fe_2O_3 0·7, P_2O_5 14·3, SiO_2 5·22, Cu 0·0009%.

According to Willstätter (Sitzungsber. K. Akad. Wiss. 1914, **12**, 402) the pigment of the cranberry is an anthocyanin (chloride, $C_{15}H_{11}O_6Cl$), a compound of galactose with cyanidin. Claassen (*ibid.* 16, 70) isolated from the fruit a bitter substance *oxycoccin* which gave reactions similar to those of arbutin.

The cowberry or foxberry closely resembles cranberry in nature and uses. Recorded analyses by Ystgaard (Tids. Norske Landwbruks. 1902, **9**, 125) give the average composition as: total solids 15·5, protein 0·25, total acids 1·92, citric acid 0·64, malic acid 0·31, sugars 6·4, pentosans 0·59, fibre 1·88%. According to Hotter (Z. landw. Versuchsw. 1906, **9**, 747) the sugars comprise glucose 3·0–4·6, fructose 4·0–5·8, sucrose 0·4–0·8% of the total dry matter.

Windisch and Schmidt (Z. Unters. Nahr.-Genussm. 1909, **17**, 584) show the average composition of the juice (sp.gr. 1·043) to be: solids 11·3, protein 0·12, acids (as citric) 1·9, invert sugar 6·5, sucrose 0·5, tannin 0·19, ash 0·3%.

Vacciniin is also present in the fruit.

Cowberry seeds, according to Diedrichs (*ibid.* 1912, **24**, 575) give the following analysis :—

Water. %	Protein. %	Fat. %	N-free extract and fibre. %	Ash. %
5·97	23·24	30·12	38·56	2·11

The seeds yield a drying oil having the following characteristics: d_{15} 0·9301, refractive index 1·4753 (25°), saponification value 190·1, iodine value 169·2, Reichert-Meissl value 0·55, Polenske value 0·30, Hehner number 95·7, acid value 1·94, hexabromides of linoleic and linolenic acids 22·8%.

A. G. Po.

CREAM OF TARTAR. Acid potassium tartrate, $C_4H_5O_6K$.

CREAMING *v.* Bleaching.

CREATINE. *Methylglycocyamine, Methylguanidinoacetic acid,*

$$H_2N{\cdot}C(NH)NMe{\cdot}CH_2{\cdot}CO_2H,H_2O,$$

discovered by Chevreul (Annalen, 1832, **4**, 293) in muscle (χρέας=flesh), occurs in human flesh, in the flesh of many warm and cold blooded animals, and in urine under certain conditions (von Liebig, *ibid.* 1847, **62**, 257 ; Gregory, *ibid.* 1848, **64**, 105 ; Schlossberger, *ibid.* 1848, **66**, 80 ; Price, *ibid.* 1850, **76**, 362 ; Voit, Z. Biol. 1868, **4**, 77 ; Marcet, J.C.S. 1864, **2**, 406 ; Folin and Denis, J. Biol. Chem. 1914, **17**, 488 ; Rose, *ibid.* 1911, **10**, 265) ; the amount varies with the species and the organ ; the flesh of fowl yields 3·21% ; of pigeon, 0·825% ; of ox, 0·697% ; of ox heart, 1·375% ; of herring, 1·324% ; and of brill, 0·614% (Gregory, *l.c.* ; Beker, Z. physiol. Chem. 1913, **87**, 28 ; according to Myers and Fine (J. Biol. Chem. 1913, **14**, 9) it is constant for a given animal.

The origin and physiological significance of creatine and creatinine are still controversial subjects of too detailed a nature to be considered here. Creatine is very unevenly distributed in the body, about 98% being found in the muscles and most of the remainder in the brain. It is not found in the urine of normal adults and cannot be regarded as a waste product of the metabolism of protein from which it is presumably formed. It is an essential substance for muscle metabolism since a large part of the creatine in muscle is present in combination with phosphoric acid as *phosphagen* (*phosphocreatine*) ; the hydrolysis and resynthesis of this compound are important phases in the processes of muscular contraction and relaxation, phosphagen thus serving as a reservoir for the inorganic phosphate necessary for the process of contraction. It is probable that creatinine is a waste product formed from creatine, although this has been disputed. For further details and references, *see* Hunter "Creatine and Creatinine," Longmans, Green & Co., 1928, Peters and van Slyke "Quantitative Clinical Chemistry," Baillière, Tindall & Cox, 1931, and Lovatt Evans "Recent Advances in Physiology," Churchill, 1930.

In order to extract creatine, the flesh is heated with its own weight of water at 60°, and the juice expressed. The flesh extract is then heated to coagulate the protein, and filtered ; the filtrate is treated with basic lead acetate until no further precipitation occurs, and again filtered after removing the excess of lead from the filtrate by sulphuretted hydrogen, when it is evaporated until creatine separates on cooling ; this is washed with alcohol and recrystallised from water (Neubauer, Z. anal. Chem. 1863, **2**, 26 ; 1867, **6**, 33). Creatine may be prepared by the decomposition of creatinine zinc chloride by means of calcium hydroxide (Benedict, J. Biol. Chem. 1914, **18**, 186).

Creatine is prepared synthetically by heating sarcosine with cyanamide at 100° :

$$CN{\cdot}NH_2+NHMe{\cdot}CH_2{\cdot}CO_2H$$
$$=NH{:}C(NH_2)NMe{\cdot}CH_2{\cdot}CO_2H$$

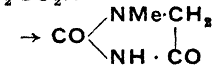
(Volhard, Z. Chem. N. F. 1869, **5**, 318 ; Strecker, Jahresber. Chem. 1868, 686) ; or, together with creatinine, by fusing sarcosine with guanidine carbonate (Paulmann, Arch. Pharm. 1894, **232**, 638). It has also been prepared by King (J.C.S. 1930, 2374) by treating sarcosine in alkaline solution with methyl*iso*thiocarbamide hydriodide. Bergmann and Zervas have obtained diacetylcreatine from sarcosine and triacetylanhydroarginine (Z. physiol. Chem. 1928, **173**, 80).

Creatine forms colourless transparent monoclinic prisms, containing 1 H_2O, which it loses at 100° ; it dissolves in 74·4 parts of water at 18° ; in 9.810 parts of cold absolute alcohol, and is insoluble in ether (von Liebig, Annalen, 1847, **62**, 257). Heat of combustion at constant pressure is 4,240 g.-cal. (Emery and Benedict, Amer. J. Physiol. 1911, **28**, 307). The presence of urea, creatinine, or certain salts raises the solubility of creatine in water and alcohol (Neubauer, *l.c.*). The aqueous solution is neutral, and has a bitter, harsh taste.

Creatine is decomposed by boiling baryta water into sarcosine, urea, and methylhydantoïn

$$NH{:}C(NH_2)NMe{\cdot}CH_2{\cdot}CO_2H+H_2O$$
$$=CO(NH_2)_2+NHMe{\cdot}CH_2{\cdot}CO_2H$$

$$CO(NH_2)_2+NHMe{\cdot}CH_2{\cdot}CO_2H$$



$$\rightarrow CO\begin{matrix} NMe{\cdot}CH_2 \\ | \\ NH\cdot CO \end{matrix}$$

(Neubauer, Annalen, 1866, **137**, 294) ; or by mercuric oxide and water into oxalic acid and methylguanidine ; or by heating with soda-lime into ammonia and methylamine. Treated with mercuric acetate in presence of sodium carbonate it yields *a-methylguanidinoglyoxylic acid,*

$$NH_2{\cdot}C(NH)NMe{\cdot}CO{\cdot}CO_2H,2H_2O\ ;$$

glistening flakes, m.p. 203–204° (Bauman and Ingvaldsen, J. Biol. Chem. 1918, **35**, 277). When potassium hydroxide is added to an aqueous solution of creatine and silver nitrate until the white precipitate first formed just redissolves, the liquid solidifies to a transparent gelatinous mass immediately reduced on heating, or in the course of a few hours at the ordinary temperature. The addition of potassium hydroxide to a solution of creatine and mercuric chloride precipitates a white crystalline compound $(C_4H_8O_2N_3)_2Hg,HgO$ (Engel, Compt. rend. 1874, **78**, 1707 ; 1875, **80**, 885). Creatine is converted into creatinine by heating with dilute mineral acids for some hours (Dessaignes, Jahresber. Chem. 1857, 544) or at 117° for 15 minutes (Benedict and Myers, Amer. J. Physiol. 1907, **18**, 362); or by boiling to dryness a solution of creatine to which has been added an equal volume of hydrochloric acid (Benedict, J. Biol. Chem. 1914, **18**, 192) ; or by heating with water only in sealed tubes at 100° for 2–3 days (Neubauer, Z. anal. Chem. 1863, **2**, 33). The equilibrium between creatine and creatinine in aqueous solutions has been studied by Edgar and Shiver (J. Amer. Chem. Soc. 1925, **47**, 1179). The ratio of the molecular concentration of creatinine to that of creatine in water at different temperatures and in various buffer solutions is given; thus in water the ratio is 0·54 at 25°; 2·89 at 100°; 36·72 at p_H 1 (50°), and 1·03 at p_H 6 (50°).

Smorodincev (J. Russ. Phys. Chem. Ges. 1915, **47**, 1275) obtained a double salt of silver nitrate and creatinine, $C_4H_7ON_3{\cdot}AgNO_3$ (decomposing 188–191°) by treating pure creatine with silver nitrate in a slightly acid solution.

Creatine forms soluble normal salts with the mineral acids (Dessaignes, Annalen, 1854, **92**, 409), and readily soluble compounds with zinc chloride, $C_4H_9O_2N_3,ZnCl_2$; and cadmium chloride, $C_4H_9O_2N_3,CdCl_2,2H_2O$ (Neubauer, *ibid.* 1866, **137**, 300). *Creatine picrate* forms woolly needles melting at 218–220° (decomp.). The m.p. is not depressed by admixture with creatinine picrate (King, J.C.S. 1930, 2374). The *flavianate* (*v.* p. 417*d*) melts at 231° (Langley and Albrecht, J. Biol. Chem. 1935, **108**, 729). When creatine in alkaline solution is treated with sodium nitroprusside and a persulphate a red colour is obtained ; Pittarelli claims that this reaction is sensitive to 1 in 50,000 (A. 1928, 1121).

Creatine is not usually estimated directly ; it is converted into creatinine (*q.v.*), and estimated as such ; for the estimation of creatine in urine, *v.* Benedict (J. Biol. Chem. 1914, **18**, 192 ; 1929, **82**, 1 ; Folin, *ibid.* 1914, **17**, 469). Methods for estimating creatine directly have been suggested by Walpole (J. Physiol. 1911, **42**, 301), who makes use of the fact that a pale red colour is given by alkaline solutions of creatine and not by creatinine when a trace of diacetyl is added, and by Lang (Z. physiol. Chem. 1932, **208**, 273) who uses the violet colour formed from creatine and acetylbenzoyl in alkaline solution. Several methods have been adapted for blood filtrates, but it is still uncertain whether the chromogenic substance in blood is really creatine, *see* Peters and van Slyke (" Quantitative Clinical Chemistry," Baillière, Tindall & Cox, 1932).

a-Guanidinopropionic acid, alacreatine,

$$NH_2{\cdot}C(NH)NH{\cdot}CHMe{\cdot}CO_2H,$$

an isomer of creatine, forms sparingly soluble prisms. It is prepared from alanine and cyanamide (Baumann, Annalen, 1873, **167**, 83) or from alanine and methyl*iso*thiocarbamide. The *picrate* forms needles, m.p. 187° (decomp.) (King, J.C.S. 1930, 2374).

The homologues of creatine are prepared by the action of cyanamide on the corresponding amino-acid in the presence of ammonia, *e.g.* *a-aminocaprocyamine,*

$$NH_2{\cdot}C(NH)NH{\cdot}CH(CO_2H)CH_2{\cdot}CHMe_2,$$

from leucine and cyanamide (Duvillier, Compt rend. 1886, **103**, 211 ; 1887, **104**, 1290). According to Duvillier (*l.c.*) methyl- or ethyl-amino-acids yield with cyanamide the corresponding *creatinine*. The *creatine* is formed only in the case of methylglycine and of *β*-methylaminopropionic acid, the latter yielding *methylalacreatine*, $NH_2{\cdot}C(NH){\cdot}NMe{\cdot}CHMe{\cdot}CO_2H$ (Lindenberg, J. pr. Chem. 1875, [ii], **12**, 253). This generalisation is not confirmed by Gansser (Z. physiol. Chem. 1909, **61**, 16), who obtained the creatinine and not the creatine from *a*-methylaminopropionic acid and cyanamide, but prepared *β-methylguanidinopropionic acid,* $NH_2{\cdot}C(NH)NMe{\cdot}[CH_2]_2CO_2H,H_2O$, m.p. 201–202°, from cyanamide and *β*-methylaminopropionic acid, and *γ-methylguanidinobutyric acid*, $NH_2{\cdot}C(NH)NMe{\cdot}[CH_2]_3CO_2H$, m.p. 307°, from cyanamide and *γ*-methylaminobutyric acid.

Formaldehyde and creatine yield the *compound* $C_6H_{11}O_3N_3,2H_2O$, decomposing at 250°, and forming a *dibenzoyl derivative,*

$$C_6H_9O_3N_3Bz_2,$$

m.p. 265–266° (Jaffé, Ber. 1902, **35**, 2896). *Phthalyldicreatine,*

$$C_6H_4[CO{\cdot}NH{\cdot}C(NH)NMe{\cdot}CH_2{\cdot}CO_2H]_2,$$

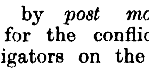
has m.p. 212° (Urano, Beit. Chem. Physiol. Path. 1907, **9**, 183). *Diacetylcreatine,*

$$NH{:}C(NHAc)NMe{\cdot}CH_2{\cdot}CO_2Ac,$$

has m.p. 165° (Erlenmeyer, Annalen, 1895, **284**, 50).

M. A. W. and W. V. T.

CREATININE. *Methylglycocyamidine,*



$$C{:}NH\begin{cases}NMe{\cdot}CH_2\\ \quad\quad\;\; |\\ NH{\cdot}CO\end{cases}$$

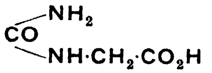
discovered by von Liebig in human urine (Annalen, 1847, **62**, 268), is also a constant constituent of the urine of horses, cows, dogs, pigs and rabbits ; the amount of creatinine in the tissues is uncertain as its determination is attended with difficulties owing to the ease with which creatine is converted into creatinine by *post mortem* autolysis. This accounts for the conflicting reports of different investigators on the creatinine content of muscle which probably contains only a very small amount if any. According to Folin and Denis (J. Biol. Chem. 1914, **17**, 487) normal human blood contains 1 mg. creatinine and 6–8 mg. of creatinine and creatine per 100 g. blood; *but see below under* Estimation of Creatinine. In domestic animals it is about the same; in birds 0·1 mg. creatinine but 11 mg. creatinine and creatine. It is probably a normal constituent of all soils (Shorey, J. Amer. Chem. Soc. 1912, **34**, 99; Sullivan, *ibid.* 1911, **33**, 2035) and vegetable matter (Oshima and Ariizumi, J. Coll. Agric. Tokyo, 1914, **6**, 17).

Under normal conditions, the excretion of creatinine is constant from day to day. The amount excreted by an individual per day varies from 7·5 to 10 mg. creatinine nitrogen per kg. body weight and is roughly proportional to his muscular development ; it is not affected by diet or exercise. Creatinine is, therefore, generally regarded as an end product of endogenous metabolism, most probably of creatine catabolism (Shaffer, Amer. J. Physiol. 1908, **23**, 1 ; Folin, *ibid.* 1905, **13**, 45, 66, 117 ; Pekelharing, van Hoogenhuyze and Verploegh, Proc. K. Akad. Wetensch, Amsterdam, 1905, **8**, 363 ; Klercker, Beit. Chem. Physiol. Path. 1906, **8**, 59 ; Folin and Denis, J. Biol. Chem. 1914, **17**, 500 ; Harding and Gaebler, *ibid.* 1922, **54**, 579 ; Hodgson and Lewis, Amer. J. Physiol, 1928, **87**, 288). Creatinine administered to animals is rapidly excreted almost quantitatively (Foster and Fisher, J. Biol. Chem. 1911, **9**, 359 ; Towles and Voegtlin, *ibid.* **10**, 479). Under ordinary circumstances no creatine is excreted by adults. Some normal women, however, all infants and young children, and adults in starvation and certain pathological conditions excrete some creatine (Denis and Minot, *ibid.* 1917, **31**, 561 ; Folin and Denis, *ibid.* 1912, **11**, 253 ; Rose, *ibid.* 1912, **10**, 265 ; 1917, **32**, 1 ; Gamble and Goldschmidt, *ibid.* 1919, **40**, 199).

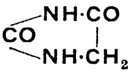
Creatinine is extracted from urine by evaporating to one-third the original volume, decanting from the salts that crystallise out, precipitating with lead acetate and filtering, removing the lead from the filtrate and precipitating the creatinine with mercuric chloride as the sparingly soluble double salt. This is separated, decomposed by sulphuretted hydrogen, and the creatinine crystallised from the filtrate as the hydrochloride (Maly, Annalen, 1871, **159**, 279 ; or by precipitating it as creatinine potassium picrate with subsequent decomposition of the double salt (Folin, J. Biol. Chem. 1914, **17**, 463 ; Benedict, *ibid.* 1914, **18**, 184).

For extraction from the body tissues and fluids, *see* Costantino (Chem. Zentr. 1915, **11**, 287, from Arch. farm. sper. 1915, **19**, 254).

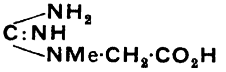
Creatinine bears the same relation to creatine as hydantoïn to hydantoïc acid



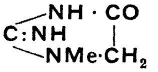
Hydantoïc acid.



Hydantoïn.



Creatine.



Creatinine.

and is prepared by boiling creatine with dilute mineral acids for some hours (Liebig, Annalen, 1847, **62**, 628) or by heating at 117° for 15 minutes under pressure (Benedict and Myers, Amer. J. Physiol. 1907, **18**, 362, *see*, however, J. Biol. Chem. 1914, **17**, 363; Folin, *ibid.* 469), or by boiling down to dryness with an equal volume of *N*-HCl (Benedict, *ibid.* 1914, **18**, 192), or by heating creatine with anhydrous zinc chloride (Edgar and Hinegardner, *ibid.* 1923, **56**, 1).

Creatinine can be prepared synthetically by heating guanidine carbonate with sarcosine at 140–160° (Horbaczewski, Maly's Jahresber. Tierchem. 1885, **15**, 86). A quantitative yield is obtained by heating N-methylglycocyamine with an organic acid (G.P. 281051, from J.S.C.I. 1915, **34**, 637).

By heating creatinine with silver nitrate and baryta in excess on the water-bath for about an hour a nearly quantitative yield of methylguanidine can be obtained (Ewins, Biochem. J. 1916, **10**, 104). By oxidation with mercuric acetate it yields α-methylguanidinoglyoxylic acid (Bauman and Ingvaldsen, J. Biol. Chem. 1918, **35**, 277).

Creatinine forms anhydrous monoclinic prisms soluble in 11·5 parts of water or 625 parts of absolute alcohol at 17° (Joppelius and Pommerehne, Arch. Pharm. 1896, **234**, 380), and separates on slow evaporation of dilute solutions in square plates containing $2H_2O$ (Salkowski, Z. physiol. Chem. 1880, **4**, 133). It is a weak base, displacing ammonia from its salts, and forming soluble salts with the mineral acids (Liebig, *l.c.*), the *picrate* $C_4H_7ON_3{\cdot}C_6H_3O_7N_3$, m.p. 212–213°, forms sparingly soluble yellow needles; the *acid picrate* $C_4H_7ON_3{\cdot}2C_6H_3O_7N_3$ has m.p. 161–166° (Mayerhofer, Wien. Klin. Woch. 1909, **22**, 90) ; the *flavianate*,[1] solubility 0·198, melts at 250° (decomp.) (Kossel and Gross, Z. physiol. Chem. 1924, **135**, 168) ; the *tartrate* $(C_4H_7ON_3)_2C_4H_6O_6$ decomposes at 207–209°; the *oxalate* $(C_4H_7ON_3)_2{\cdot}C_2H_2O_4$ is sparingly soluble in alcohol (Poulsson, Chem. Zentr. 1904, ii, 30). Creatinine forms characteristic double salts, with platinic chloride,

$$(C_4H_7ON_3,HCl)_2{\cdot}PtCl_4,$$

orange-red plates, m.p. 220–225° ; with auric chloride, $C_4H_7ON_3{\cdot}HCl{\cdot}AuCl_3$, yellow crystals, m.p. 170–174° ; with potassium picrate, $C_4H_7ON_3{\cdot}C_6H_3O_7N_3{\cdot}KC_6H_2O_7N_3$, lemon-yellow prisms, 100 parts of water dissolve 0·1806 part of the salt at 19–20° ; with zinc chloride, $(C_4H_7ON_3)_2{\cdot}ZnCl_2$, almost insoluble in alcohol (Heintz, Jahresber. Chem. 1847, 48, 883) ; with mercuric chloride,

$$4(C_4H_5HgON_3{\cdot}HCl){\cdot}3HgCl_2,2H_2O$$

(Johnson, Proc. Roy. Soc. 1886, **43**, 493).

Creatinine is converted into creatine by the action of cold dilute ammonia or calcium hydroxide solutions ; or on treatment with iodine (Reichardt, Pharm. Ztg. 1911, **56**, 922) ; boiling baryta solution converts it into ammonia and methyl hydantoïn ; with alkaline oxidising agents it yields methylguanidine and oxalic acid, but is comparatively stable towards acid permanganate solutions (Jolles, Ber. 1902, **35**, 160).

The presence of creatinine in dilute solution or in urine can be detected by (1) Weyl's test (Ber. 1878, **11**, 2175), which consists in the production of a ruby-red coloration, changing to yellow when, to a solution of creatinine, a few drops of 10% sodium nitro-prusside and the same quantity of 10% sodium hydroxide or carbonate solution are added. On acidifying the

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[1] " Flavianic acid " is the name applied by the authors to naphthol yellow S, 1-naphthol-2 : 4-dinitro-7-sulphonic acid.

solution with acetic acid the colour is discharged, turning to green or blue on boiling due to the formation of Prussian blue (Salkowski ; Colasanti, Gazzetta, 1887, **17**, 129). Guareschi (Ber. 1888, **21**, Ref. 372) has shown that this reaction is given by compounds other than creatinine containing the —CO·CH$_2$— group. (2) Jaffé's test (Z. physiol. Chem. 1886, **10**, 399) is the production of a deep-red colour, when picric acid and an excess of sodium hydroxide solution are added to the liquid containing the creatinine. It is now generally accepted that the red colour in Jaffé's reaction is not due, as suggested by Chapman (Chem. News, 1909, **100**, 175), to sodium salts of picramic acid and diaminonitrophenol formed by reduction of the picric acid by the creatinine, as the red compound has been isolated and shown to be a red tautomer of creatinine picrate although its structure is still under discussion (Greenwald, J. Biol. Chem. 1924, **59**, 601 ; 1928, **80**, 103 ; 1930, **86**, 333 ; Anslow and King, J.C.S. 1929, 1210).

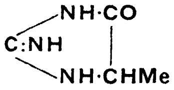
Estimation of Creatinine.—The older methods for the estimation of creatinine were based upon the isolation of the base in the form of its sparingly soluble double salt with mercuric or zinc chloride, and either weighing the precipitate or estimating the metal or the nitrogen in the compound (Neubauer, Annalen, 1861, **119**, 35; Salkowski, Z. physiol. Chem. 1886, **10**, 113; Grocco, Chem. Zentr. 1887, **17**; Kolisch, *ibid.* 1895, i, 814; Ladd and Bottenfield, Amer. Chem. J. 1898, **20**. 869). Edlefsen (Chem. Zentr. 1909, i, 108) recommends precipitating the sulphate in the presence of alcohol and ether, dissolving it in water, and titrating the solution with standard barium hydroxide solution, using phenolphthalein as indicator.

The method generally adopted for estimating creatinine in urine is Folin's colorimetric method, based on Jaffé's reaction (Z. physiol. Chem. 1904, **41**, 223; J. Biol. Chem. 1914, **17**, 469). If creatine is also present in the urine the *total creatinine* is determined after converting the creatine into creatinine by heating with acid. Subtraction of the preformed creatinine, determined separately, gives the creatine as creatinine. The conversion of creatine into creatinine may be carried out by (1) boiling with a saturated solution of picric acid, and this method must be used if glucose is present (Folin, *l.c.*) ; (2) autoclaving with saturated picric acid (Folin, *l.c.*) ; or (3) boiling down to dryness with hydrochloric acid in the presence of metallic lead (Benedict, J. Biol. Chem. 1914, **18**, 191). It is important that pure picric acid should be used for the colorimetric determination of creatinine by any method involving Jaffé's reaction (Folin and Doisy, *ibid.* 1917, **28**, 349). Benedict gives suitable methods for the purification of picric acid for this purpose (*ibid.* 1922, **54**, 239; 1929, **82**, 1).

The presence of creatinine in blood still remains to be established with certainty. Whilst there is a chromogenic substance which can be estimated by Folin's method (Folin and Wu, *ibid.* 1919, **38**, 81) it is probably in the main not creatinine (Behre and Benedict, *ibid.* 1922, **52**, 11 ; and *see below*).

More recently a new colorimetric method has been employed for the estimation of creatinine in urine. This consists in treating the urine with alcoholic 3:5-dinitrobenzoic acid and 6% sodium hydroxide. Creatine, glucose and ketones (in usual amounts) do not interfere. The application of the method to blood supports the view that the chromogenic substance is not creatinine (Benedict and Behre, *ibid.* 1936, **114**, 515 ; Langley and Evans, *ibid.* **115**, 333).

An isomeride of creatinine, *alacreatinine*,

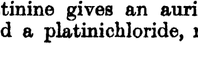


was prepared (Ber. 1873, **6**, 1371), and other isomerides have been described by Korndörfer, Arch. Pharm. 1904, **242**, 620 ; Schenck, *ibid.* 1910, **248**, 376; 1911, **249**, 463 ; Schmidt, *ibid.* 1910, **248**, 568. Johnson and Nicolet (J. Amer. Chem. Soc. 1915, **37**, 2417) obtained two methylglycocyamidines isomeric with creatinine by the action of methylamine on the ethyl ester of benzoylpseudoethylthiohydantoic acid and debenzoylating.

Two isomeric *nitrosocreatinines* were obtained by Dessaignes (Annalen, 1856, **97**, 341) and Märcker (*ibid.* 1865, **133**, 305), by passing the nitrous fumes from the action of nitric acid on arsenious oxide into an acid solution of creatinine. The less soluble *a-nitrosocreatinine*, $C_4H_8O_2N_4$, decomposes at 210°, forming a colourless liquid that quickly solidifies to a brown mass from which a new *base*, $C_7H_{12}O_2N_{10}$ can be extracted ; it forms a crystalline *nitrate*, *hydrochloride* and *platinichloride*, and yields the *bromo-derivative* $C_4H_7O_2N_4Br$. The more soluble *β-nitrosocreatinine*, $C_4H_8O_2N_4$, melts at 195° to a brown liquid and decomposes at 220°.

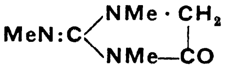
According to Kramm (Chem. Zentr. 1898, i, 37), the yellow colour formed by the interaction of sodium nitroprusside and sodium hydroxide on creatinine (*cf.* Weyl, Ber. 1878, **11**, 2175), is due to the formation of a *nitrosocreatinine*, $C_4H_6O_2N_4$, which can be isolated as a colourless crystalline precipitate by adding acetic acid to the yellow alkaline solution and shaking vigorously. According to Schmidt and Hennig (Arch. Pharm. 1912, **250**, 345) this is an oxime ; they find that on treatment with sodium nitrite in nitric acid solution creatinine yields a mixture of methyl hydantoïn oxime, m.p. 193–194°, and creatinine oxime, which begins to discolour at 250° but does not melt.

The following *acyl-* and *alkyl-* derivatives of creatinine have been prepared : *Benzoylcreatinine*, $C_{11}H_{11}O_2N_3$, pale yellow needles, m.p. 187° (Urano, Beitr. Chem. Physiol. Path. 1907, **9**, 183) ; *methyl, dimethyl*, and *trimethyl creatinine* and salts (Korndörfer, Arch. Pharm. 1904, **242**, 641 ; Kunze, Arch. Pharm. 1910, **248**, 578). Methylcreatinine

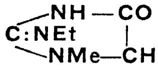


gives an aurichloride, m.p. 170–171°, and dimethylcreatinine gives an aurichloride, m.p. 128–129°, and a platinichloride, m.p. 177–179°.

According to Kunze the constitution of dimethylcreatinine is



it reacts as a tertiary base ; *ethylcreatinine*



(Neubauer, Annalen, 1861, **119**, 50), *see* Henzerling (Arch. Pharm. 1910, **248**, 594 ; the *platinichloride* crystallises in monoclinic plates, m.p. 197–211° ; *ethylcreatinine hydriodide*, m.p. 217–219° ; *diethylcreatinine platinichloride* 201–202°).

For various other substituted derivatives of creatinine, *see* Duvillier (Compt. rend. 1882, **95**, 456 ; 1883, **96**, 1583 ; **97**, 1486 ; 1885, **100**, 916 ; 1886, **103**, 211 ; 1887, **104**, 1290) and Greenwald (J. Amer. Chem. Soc. 1925, **47**, 1443).

M. A. W. and W. V. T.

CREOLINE. A coal tar disinfectant prepared from coal tar creosote, contains 45–60% neutral oils, 10–15% phenols, 30–40% rosin soap.

CREOSOL (4-hydroxy-3-methoxy-1-methylbenzene) *v.* CREOSOTE.

CREOSOTAL (creosote carbonate) is a mixture of carbonates of the various phenols contained in creosote, chiefly creosol, guaiacol, and cresols.

It may be prepared by heating creosote with a benzene solution of phosgene under pressure, but is generally produced by passing a stream of phosgene into a solution of creosote in aqueous caustic soda. Creosotal separates as an oil and is washed with dilute caustic soda solution and then with water. It contains the equivalent of about 90% of creosote.

Creosotal is a clear, colourless or yellowish, viscid liquid, insoluble in water but soluble in alcohol, ether, chloroform, benzene, etc. (Aufrecht, Pharm. Ztg. 1908, **53**, 480). It is neutral, has little odour and only a slight taste of creosote. Crystals of guaiacol carbonate may settle from samples after long standing or on freezing. Boiling with alcoholic caustic alkali gives creosote and alkali carbonate.

It has to some extent replaced creosote in the treatment of pulmonary tuberculosis, bronchitis and pneumonia.

CREOSOTE. Tars obtained by the destructive distillation of wood and of coal in retorts, coke ovens, or blast furnaces, when subjected to distillation yield fractions technically known as " creosote," and which find extensive and important uses in the industrial arts, the most important type being that derived from gas works or coke oven coal tar.

The term " kreosote " was originally applied to the product obtained from wood tar. The increase in production and distillation of coal tar with the extension of the use of the creosote oil so obtained for the preservation of wood resulted in the terms creosote and creosote oil being used commercially as meaning the heavier distillates from gas works and coke oven tar, the oils from other tars being distinguished by a prefix to indicate their origin, as " blast-furnace creosote." In pharmacy the term creosote is still retained for wood creosote.

WOOD-TAR CREOSOTE.—The tar derived from the distillation of beechwood and other hard woods, when subjected to further distillation, yields certain fractions that are heavier than water. These are agitated with an aqueous solution of caustic soda, which is then separated from insoluble oils, boiled with free access of air, in order to oxidise various impurities present and to distil off hydrocarbons, and then decomposed with dilute sulphuric acid or carbon dioxide. The crude creosote which separates is again submitted to treatment with alkali and acid, and finally distilled, the fraction distilling between 200° and 230° being collected separately.

Wood-tar creosote, when freshly prepared, is a colourless, transparent liquid of an oily consistency, and which retains its fluidity at a very low temperature ; its sp.gr. varies from 1·037 to 1·087 ; it distils between 200–230°, and dissolves in about 200 parts of water ; its odour is strong and penetrating, resembling that of wood smoke ; it has a high refractive index (1·51) and burns with a luminous smoky flame. It is neutral or only faintly acid to litmus. It is powerfully antiseptic, but does not coagulate albumin ; is not so caustic as carbolic acid and relatively less poisonous. Wood creosote is essentially a mixture of the ethers of the polyhydric phenols, chiefly guaiacol (*o*-methoxy phenol, b.p. 205°) and creosol (2-methoxy-4-methyl phenol, b.p. 221°) ; whilst phenol, *o*-, *m*- and *p*-cresols, *o*-ethyl-phenol and xylenols may be present in varying amounts. The presence of the dimethyl ethers of pyrogallol (b.p. 262°) and of methyl–and propyl–pyrogallol (b.p. 265° and 285°) has been identified in samples. Dimethylguaiacol (b.p. 230°) and propylguaiacol (b.p. 241°) are present in insignificant amounts. The latter is objectionable in the medicinal grade, since a single drop on the tongue causes bleeding ; its presence may be recognised by the blue coloration produced with baryta water.

The percentage composition of beechwood and oak creosotes, freed from hydrocarbons, is given by Béhal and Choay (Compt. rend. 1894, **119**, 166) as follows :

	Beech.	Beech.	Oak.
Distillation temp. °C.	200–220°	200–210°	200–210°
Specific gravity .	1·085	1·085	1·068
Mono-phenols . .	39·0	39·0	55·0
Guaiacol . . .	19·7	26·5	14·0
Creosols and homologues . . .	40·0	32·1	31·0
Loss	1·3	2·4	—

Wood creosote is miscible in all proportions with alcohol, ether, glacial acetic acid, benzene, carbon disulphide and light petroleum spirit. It dissolves in concentrated sulphuric acid to a red liquid, which slowly changes to purple-violet ; it is violently attacked by nitric acid, is soluble in aqueous solutions of alkali hydroxides, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide. On the other hand, it is practically insoluble in strong ammonia. Official in Brit. Pharm. 1932, sp.gr. at 15·5° not below 1·070, commencing to distil at about 200°, and yielding not less than 95% between 200° and 230°; 2 c.c. should require 10–18 c.c. N-NaOH to produce a clear solution, and the liquid should remain clear on dilution with 50 c.c. of water (limit of hydrocarbons, and of bases). Owing to the demand for guaiacol for pharmaceutical purposes, much of the wood creosote now sold is frequently found to have been deprived of part or the whole of the guaiacol it contained. Methods for the determination of guaiacol in wood creosote are given by Béhal and Choay (Compt. rend. 1893, **116**, 197); Kebler (Amer. J. Pharm. 1899, **71**, 409). Wood-tar creosote is distinguished from coal-tar phenols by its reaction with an ether-alcohol solution of nitrocellulose (equal parts), no coagulation being produced.

Wood creosote is used as an antiseptic and analgesic material (external), and internally in the treatment of tuberculosis by preparations such as creosote carbonate and the lactic acid and valerianic esters. Also employed in the preservation of mine timbers, in lignin removal from jute fibre, and in ore flotation. Bube (B.P. 257151) employs aq. ethyl alcohol at 50°C. for extraction of phenols from wood tar. The alcoholic extract of brown coal tar has been placed on the German market under the name *Fresol*—this product has sp.gr. 1·01–1·04, viscosity at 20°C., 5–10° Engler, flash-point 100–110°, constituents sol. in 38° Bé NaOH, 60–90%, colour black. Graefe (G.P. 232657) extracts with alcohol in a continuous column apparatus—against saving in chemicals over older methods is to be placed a loss of only 0·3–0·5 parts alcohol on 100 parts of tar.

Coal-Tar Creosote.—The creosote oils derived from coal tars (*cf.* Coal Tar) may be divided into two main classes—light creosote being the fraction distilling mainly between 190° and 235°, and ordinary creosote oil, chiefly employed for timber preservation, and distilling mainly between 200° and 300° to 350°C. The light creosote normally consists of the middle or carbolic oil fraction obtained in the primary distillation of the tar, the crystallisable naphthalene having been removed by cooling the oil to atmospheric temperatures. If the oil has been treated for the recovery of phenols, the residual content of these compounds may be 3–10%. If the oil is to be employed for disinfectant and sheep dip manufacture the cresol content may rise to 40% (so-called cresylic creosotes). The ordinary creosote contains the oils distilling from the tar between the end of the carbolic oil or naphthalene oil fractions and the pitch, and usually at the present time no individual component is removed. Improved methods of tar distillation yielding close-cut fractions have made possible the isolation of other pure products, and in Germany acenaphthene, a raw material for the production of dyestuffs of the thio-indigo series, has been recovered from the 265–275° fraction, and indole from the 240–260° fraction (G.P. 223304). Formerly the oil distilling between 300° and the end of the distillation was separately collected, cooled, and the clear oil (filtered anthracene oil or green oil) separated from the crystalline crude anthracene. The crude anthracene was purified to yield a high-grade anthracene and carbazole, and the fluid oil was sold for the preservation of timber by brush treatment (*carbolineum v. infra*). A fall in the demand for anthracene, owing to the anthracene derivatives for the dyestuffs industry being more simply obtained synthetically, coincided with a growing difficulty in obtaining anthracene of low paraffin (*n*-nonadecane) content from many modern types of tars, and at present in the United Kingdom the anthracene oil fraction is frequently run direct to the creosote storage wells.

Composition: So many varying factors influence the composition of creosote oils that it is impossible to give more than the following general list of some of the more important compounds that have been found to be present in the samples examined: *hydrocarbons*—naphthalene, α- and β-methylnaphthalenes, 1:6-, 2:3-, 2:6-, 2:7-, dimethylnaphthalenes, anthracene, and β-methylanthracene, phenanthrene, diphenyl and its methyl and dimethyl homologues, acenaphthene, 4·5-benzoindane, fluorene together with varying amounts of saturated and unsaturated hydrocarbons of the aliphatic series; *oxygen-containing compounds*—phenol homologues, chiefly cresols and xylenols, α- and β-naphthol, diphenylene oxide and its methyl derivative; *nitrogen-containing compounds*—pyridine and its methyl and dimethyl homologues, aniline and toluidine, quinoline and *iso*quinoline and their methyl and dimethyl homologues, α- and β-naphthylamine, acridine, carbazole, indole and its methyl homologues; *sulphur-containing compounds*—phenylthiol, thionaphthene, thiodiphenylene. The oils from vertical retort tars contain a higher proportion of aliphatic hydrocarbons than those obtained from horizontal retort and coke oven tars, and this is indicated by the lower specific gravity of the close-cut fractions obtained by redistillation.

Physical Properties: The latent heats of evaporation of tar distillates have been determined by Weiss (Ind. Eng. Chem. 1922, **14**, 72) fraction 249–296°C., 146 B.Th.U.'s per lb.; 296–345°, 153; 345–392°C., 132; 392–438°C., 117. Specific heat of tar distillates 0·34±0·04 at 15–90°C. (International Critical Tables), 0·4 at 40°, 0·5 at 80°, 0·6 at 135°C. (Krebs, Gas- u. Wasserfach, 1930, **73**, 824). Calorific value horizontal retort tar-oil, sp.gr. 1·049 at 20°C., 16,544 B.Th.U./lb. gross, 15,863 B.Th.U./lb. net; vertical retort tar-oil, sp.gr. 1·016 at 20°C., 16,540 B.Th.U./lb. gross, 15,772 B.Th.U./lb. net; blast-furnace tar-oil, sp.gr. 0·903, 17,986 B.Th.U./lb. gross, 17,286 B.Th.U./lb. net (Moore). The sample of horizontal retort tar-oil examined contained 14% phenols, water 0·6%, and gave on analysis carbon 89·7, hydrogen 7·4, oxygen + nitrogen 2·25, sulphur 0·65%. The vertical retort tar-oil sample contained 28% tar acids, water 0·7%, and carbon 85·75, hydrogen 7·92, oxygen+nitrogen 5·14, sulphur 0·49%. The gross calorific value of horizontal retort tar-oil has been given as 9·900–50T cals., where T is the percentage of phenols present. Coefficient of expansion is 0·00075 per deg. C.

Commercial Uses and Grades.—Creosote finds its largest application in the preservative treatment of timber, especially railway sleepers, telegraph poles, and marine piling, against fungi, white ants, and marine borers respectively. The resistance to mechanical forces is also improved by creosoting. The largest consumer, the United States of America, uses annually upwards of 100 million Imperial gallons, 180 million gallons being used in the peak year, 1929. In 1935 the U.S.A. production was 90 million gallons; in 1936 34 million gallons were imported, of which 20 million gallons came from the United Kingdom. Formerly the U.S.A. absorbed 50% of the British production, but from 1929 the British export figure to U.S.A. fell owing to the increased American production, and reached a minimum at 9 million gallons in 1932. No official figures for the United Kingdom are available, but the production of creosote oils of all grades for the year 1935 and 1936 is estimated at 80 and 85 million gallons respectively, the use figure for timber treatment at 12–14 million gallons per annum, and the total export figures for 1935 and 1936 are 23½ and 36½ million gallons respectively.

For estate timber, fluid creosotes may be applied by brush or spray, or the posts, etc., may be immersed in the oil at 180°F. contained in open tanks, and allowed to cool while still immersed. The more effective method is to apply the creosote oil under pressure, steel cylinders 75 to 105 ft. in length by about 7 ft. in diameter being employed. In the Bethell "full-cell" process, the timber is subjected to a vacuum of 22 inches for 30 minutes, and the oil at a temperature of 180–210°F. is then introduced without breaking the vacuum until the cylinder is full. The pressure is then raised to 100 to 200 lb. per sq. in., and when absorption is complete the surplus oil is run off and a vacuum may be applied for 15 minutes (Lowrie modification). Green timber may be conditioned by a preliminary heating for 24 hours in the oil under vacuum, maximum temperature 200°F., to remove the surplus water (Boulton process). In the Rueping "empty-cell" process the timber is subjected to an initial pressure of 10 to 60 lb. per sq. in., and the oil is then introduced into the cylinder, the pressure being maintained constant. The pressure is then raised to 80 to 120 lb. per sq. in. to give maximum injection. The amount held in the timber is then reduced to the required figure by expansion of the air initially introduced and by the application of a high vacuum for a short period. Absorption figures are of the order of 15 to 20 lb. per cu. ft. and retention 7 to 10 lb. per cu. ft. In the Card process, zinc chloride and creosote are employed, typical absorption figures being ½ lb. zinc chloride and 3 lb. of creosote per cu. ft.

The quantity of oil absorbed depends upon the species, growth and size of the timber, the creosoting process employed, and the admissible cost. Penetration of the oil may be assisted by incising, that is, by making a number of small cuts over the surface of the timber parallel to the grain and about ¾ in. deep by 1 in. long. The usual figures lie between 6 and 20 lb. per cu. ft. The life of the timber is raised from 3 to 6 years to 25 years and upwards, dependent upon the conditions of employment, such as climate, location, mechanical stresses, etc.

The desirable properties in a creosote oil are toxicity, permanency and power of penetration and waterproofing. Considerable laboratory work on the relative toxicity of the constituents and fractions of coal tar creosote has not led to conclusive results. The more important standard specifications are as follows: B.S.. 144/1936, Type A, calls for an oil sp.gr. $^{38}_{20}$ 1·010–1·065; completely liquid on warming to 38°C., and on cooling remaining completely fluid after standing 2 hours at 32°C.; water content not more than 3%; yielding on distillation to 205°C. maximum 6%, to 230°C. maximum 40%, to 315°C. maximum 78 w/w%, residue above 315° soft and not sticky; phenols 5–16%; matter insoluble in benzole maximum 0·4%. Type A2 admits an oil of sp.gr.$^{38}_{20}$ 0·995–1·065, the other clause being as before, except that no maximum is specified for the phenol content and the maximum allowable distillate at 315° is 85%. Type B covers creosote from coal-tar made in Scotland, the details being as for Type A2. Creosote from low temperature tar is admitted under type A2, with a minimum specific gravity 0·935, and blast furnace creosote under type B with similar limits. Creosote required for brush application should be fluid on cooling and standing at 15·5°C. for 2 hours. For the distillation test a standard side arm flask and thermometer graduated for 100 mm. immersion are employed. The American Railroad Engineers Specification for No. 1 grade oil is sp.gr.$^{38}_{15\cdot5}$ not less than 1·03; water maximum 3%; matter insoluble in benzole maximum 0·5%; distillate on a water-free basis up to 210° maximum 5%, to 235° maximum 25%; coke residue maximum 2%. The distillation test uncorrected for barometric pressure is performed in a special standard flask, a total immersion thermometer being employed. The American Railroad Engineers Association oil in general meets the continental specifications, except that in Scandinavia and Germany the maximum distillate to 235° is limited to 20%, and a phenol clause is included (Scandinavia, 3–8%).

Commercial oils are sometimes diluted with oil-gas tar and its distillates, or with mineral oils; these mixtures have a lower conservation value. In America coal-tar creosote solutions are employed, of which at least 80% is a distillate from coal-gas or coke-oven tar, and the remainder refined or filtered coke-oven tar. The standard American Wood-Preservers Association specification is sp.gr.$^{38}_{15\cdot5}$ 1·05–1·12; water maximum 3%; distillate on a water-free basis to 210° maximum 5%, to 235° maximum 25%; matter insoluble in benzole maximum 2%; coke residue maximum 6%. *Literature.*—Proceedings of British and of American Wood-Preservers Associations.

Carbolineum is a fluid, high-boiling, tar-oil, distilling maximum 10% at 250°C; sp.gr. at 20° 1·08–1·11; phenols maximum 10%; water maximum 1%.

The A.R.E.A. Specification for anthracene oil covers an oil of sp.gr.$^{38}_{15\cdot5}$ 1·09–1·13; distilling not more than 1·5% to 235°, 16·5% to 300°, 45% to 355°; water maximum 0·5%; coke residue maximum 2%.

Other outlets for creosote oil are:

Disinfectants and Sheep Dips.—An oil suitable for disinfectant manufacture should have sp.gr. 0·95–1·00 and distil mainly between 200° and 300°. The oil should be free from crystallisable naphthalene at 5°C., and the tar acid content (mainly cresols) will vary with the type of product required. Oils yielding pink emulsions are not favoured for sheep dips.

Fuel Oil for Furnace Work, particularly in the metallurgical and glass industries, is fed through atomising burners operated by compressed air, and should normally have specific gravity not exceeding 1·07 at 38°C.; water content not exceeding 1·0%; flash-point not below 150°F. (*cf.* B.S. 503/1933).

The above oil may require steam-heated storage and pipe lines, which serve not only to prevent separation of naphthalene or anthracene, but also to lower the viscosity and improve atomisation in the burner. Alternatively, the creosote may be mixed with oil-gas tar, dehydrated coal-tars, or with petroleum fuel oils. In blending with oils of specific gravity below unity, the specific gravity of the mixture requires careful attention to avoid mixtures of unit specific gravity. Owing to the high carbon and low hydrogen content, the heat lost in flue gases is low. The gross calorific value is of the order of 16,500 B.Th.U. per lb. The removal of phenols from tar-oils raises the calorific value by about 35 B.Th.U. per lb. for each 1% removed. On the Continent a mixture of 80% tar oil and 20% pitch has been employed, specification being flash-point (Pensky-Martin) minimum 75°C. (open); viscosity maximum 8° Engler at 20°; no deposit at 8°C. for 2 hours; free carbon maximum 4%; calorific value 8,500 g.-cal. minimum.

Spark Ignition Engine Fuel.—Considerable attention has been directed to this potential market. Creosote oil can be used with a greater thermal efficiency than petrol, but preheating of the oil entering the cylinder is necessary, and the employment of a volatile hydrocarbon fuel is necessary for starting up the engine, and for use when idling. Advance has been made in the design of suitable dual carburettors, but the results have not fulfilled expectations (Inst. Gas Eng. Report, 1934). The creosote oil should be free from crystallisable naphthalene at the prevailing atmospheric temperatures, should distil almost wholly below 265°C., the water content should not exceed 0·50%; phenols maximum 10%; and the coke value (Conradson test) should not exceed 0·1%. An alternative fuel is obtained by admixture of the creosote oil with up to 20% of crude benzole or solvent naphtha. These fuels have a high anti-knock value and are suitable for engines of high compression ratio, but crank case dilution is high and plug gumming troubles are difficult to overcome.

Compression Ignition Engine Fuel.—Creosote oils were used during the period 1914–1919 in this country and in Germany for large stationary Diesel engines. In 1929 the German consumption still amounted to 16,000 tons. Creosote oil has a high spontaneous ignition temperature (440–490° in oxygen) and modifications in engine design are necessary to ensure satisfactory running. Improved nozzles and flame plates to give fine atomisation have led to success. The compression should not be less than 480 lb. per sq. in., the fuel admission must be advanced and pilot jet ignition employing a petroleum distillate normally 2 to 4% of the total fuel at full load, is used. Although slight modification to slow-speed Diesel engines may overcome difficulty of high ignition temperature, this property, together with long ignition delay of tar fuel oils, renders them unsuitable for employment in the modern high-speed engine of the Diesel type. It has been shown that the phenols are partly responsible for the high ignition temperatures, but their removal does not reduce the ignition temperature to a figure comparable with that of the petroleum Diesel oils. Blending with shale oils, paraffin oils, and synthetic oils (Glückauf, 1936, **29**, 697) has given promising results, and the cetene number of creosote oils has been raised from about 15 to a satisfactory figure of the order of 45 by the addition of 30% and upwards of these oils. Experimental work employing added primers, substances of low spontaneous ignition point such as trinitro-resorcinol, methyl nitrate, hydrazine perchlorate, nitroxyl ethylene chlorhydrin, etc., has not yet yielded useful results, partly due to cost (*cf.* B.P. 436027, 461320; G.P. 574678, 612073). Successful results are claimed by the employment of an insulated catalyst contact mass (thorium oxide or platinum on asbestos wool or vanadium pentoxide supported on silica gel) built into the pre-combustion chamber of the engine in the path of the atomised oil. It has been shown that tar-oils which give a Moore ignition temperature in oxygen of 440–470° give ignition temperatures of 165–180° in the presence of platinum on asbestos, the normal figure for American gas-oil being 248°C. (Glückauf, 1932, **68**, 980). Developments in design, including better atomisation and increased temperature of fuel either within or prior to the combustion chamber, may produce an engine that is less fuel-sensitive. A suitable oil may have the following characteristics: fluid at prevailing atmospheric temperatures, water below 1%, and preferably 0·5% or lower; distillation test minimum 60% at 300°C.; matter insoluble in xylol maximum 0·2%; coke residue (Conradson test) maximum 3·0%; ash maximum 0·02%; flash-point minimum 65°C.; viscosity maximum 3° Engler at 20°C. Some users specify maximum phenols content 10%, maximum sulphur content 0·5%, and chlorine maximum 0·02%.

Benzole Wash Oil to be employed for the recovery of benzole from town and coke-oven gas should have sp.gr. at 15°C., 1·01–1·035; distillation test nil at 200–210°C., not less than 70% at 300°C.; phenols normally 7–10%, but it is generally agreed the lower the better; water maximum 1%. The crystallisable content of naphthalene is usually specified as nil on cooling the oil to 55°F., or may be limited to 7% on cooling to 45°F. the fraction distilling to

300°C. Krebs (Gas- u. Wasserfach, 1930, **73**, 824) gives distillation test nil at 200°C., 90% below 300°, the distillation curve to be as nearly linear as possible. The presence of anthracene is undesirable. Viscosity of fresh oil is 1·5° Engler at 20°C., the spent oils have a viscosity of 8° and upwards. For data on absorptive capacity of oils, *see* "Motor Benzole" (Hoffert and Claxton).

Hydrogenation.—By treatment at elevated temperatures (440–500°C.) and in presence of hydrogen under high pressure (200–265 atmos.) the rate of reaction being accelerated by catalysts (molybdenum sulphide, or oxide, zinc oxide, and magnesium oxide on active carbon or silica gel), creosote from high and low temperature tars undergoes hydrogenation-cracking to yield lower boiling spirits of increased hydrogen-carbon ratio. Crude low temperature tar may also be used as raw material. Tar-oils of appropriate distillation range (*i.e.* not distilling above 300–325°) may be treated directly in the vapour phase, but tars need preliminary treatment in the liquid phase and are fed to the plant with the coal where this is being treated. The Billingham plant, which started operations January, 1935, is stated to have been designed to handle annually 10,000 tons low temperature tar, 40,000 tons coal tar creosote, 100,000 tons coal. The following figures are given by King and Cawley (J. Inst. Petroleum Tech. 1936, **22**, 601):

	Creosote.	Low temp. tar.	Low temp. tar oil.	Petroleum. Diesel oil.	Gasoline produced.
Carbon %	87·0	82·0	82·0	86·0	85·7
Disposable hydrogen %	6·7	6·9	7·9	12·2	14·3
Mol. ratio	0·92	1·01	1·17	1·7	2·0

Yields of gasoline on complete conversion are of the order of 80 to 90% by weight or just over 100% by volume. The octane value and other properties of the spirit depend upon the operating conditions; for further information, *see* Gordon (J. Inst. Fuel, 1935, **9**, 69), King *ibid.* 1936, **9**, 323), Smith (Engineer, 1936, **161**, 619, 659).

Flotation processes for the concentration of certain minerals, particularly sulphide ores, are important and widely used. A mixture claimed to give good results is pine oil 10%, coal-tar creosote 80%, coal tar 10%—the quantity of flotation oil employed is 1–3·5% by weight of the mineral treated. The content of phenols in the grade used should be kept constant.

Grease Making.—Attempts have been made to employ the oils distilling above 300°C., freed from crystalline matter and having a viscosity 2–3·5° Engler at 50°C. as a home source of lubricating oils. A tendency to resinify and a high rate of viscosity change with temperature are serious disadvantages (Bruhn, Stahl u. Eisen, 1919, **39**, 402, 469; Broche, Glückauf, 1932, **68**, 965). These oils have been employed as a sealing oil in waterless gasholders. They are also employed in the production of axle greases, the oil being mixed with slaked lime and rosin oil.

Brick Oil.—A heavy fluid creosote of sp.gr. 1·06–1·08 at 60°F.

Lamp (*Flame*) *Black* is manufactured by partial combustion of the oil in a limited air supply. The yield is according to the carbon content of the oil and the design of the burner and condensing plant; normally the figure for a mixture of naphthalene and anthracene oils is 60 to 70%. Coarse and fine grades are obtained by fractional separation in the chambers through which the gases pass.

LOW TEMPERATURE TAR CREOSOTE.—These oils are obtained from tars produced by carbonising bituminous coking coals at temperatures below 600°C. The hydrocarbons present are more closely related to petroleum (paraffin and naphthene series) than to the gas-tar oil hydrocarbons, being of low specific gravity, naphthalene in recoverable quantities being absent, and the higher boiling fractions contain paraffin wax. The unwashed oil contains a high percentage of phenolic bodies (cresols and higher homologues) and of other bodies soluble in aq. NaOH. For fuller information on constitution, *see* G. T. Morgan (J.S.C.I. 1928, **47**, 131T) and Fuel Research Dept. papers.

Low temperature tars may be directly hydrogenated to yield an equal volume of motor spirit or the tar may be submitted to distillation and refining processes to yield fractions suitable for employment as Diesel engine fuels, furnace fuel oils, timber-preserving oils, or for manufacture of disinfectants. Typical analyses of oils from Coalite process low temperature tar (*see* Bristow, J. Inst. Petroleum Tech. 1936, **22**, 583) are:

Diesel Oil.—A fraction distilling mainly between 200° and 300°C. which has been carefully washed and redistilled, and to which 2% of primer has been added, sp.gr. 0·916 at 60°F.; closed flash-point (Pensky-Martin) 166°F.; viscosity (Redwood No. 1) at 100°F. 31 seconds; coke 0·08%; cold test at 0°F. fluid; total sulphur 0·91%; spontaneous ignition temperature in oxygen 255°C. . phenols nil; calorific value gross 18,450, nett 17,269 B.Th.U. per lb.

Fuel Oil.—(*a*) Sp.gr. 0·983 at 60°F.; water 0·3%,; open flash-point (Pensky-Martin) 212°F.; fire-point (Pensky-Martin) 255°F.; viscosity (Redwood No. 1) at 70°F. 81 seconds, 100°F. 50 seconds; initial and final boiling-points respectively 207° and 400°C. (91·5%); crude phenols 2·5%; calorific value 18,275 B.Th.U. per lb.; sulphur 0·78%.

(*b*) An unwashed grade has sp.gr. 1·0085 at 60°F.; closed flash-point (Pensky-Martin) 186°F.; viscosity (Redwood No. 1) at 60°F. 53·5 seconds; distillate to 300°C. 72%; crude phenols 50%; calorific value 16,848 B.Th.U. per lb.; sulphur 0·70%.

Timber-Preserving Oil.—A fraction to comply with B.S. 144/1936, has been placed on the market and detailed investigations of the wood preserving properties of this oil are being made. A type analysis is sp.gr. 38°C. 0·995; distillate to 205° 1·8, to 230° 18·3, to 315°

65·3%; phenols and compounds soluble in aq. $NaOH$ in distillate to 315°C., 46%.

Oil for Disinfectant Manufacture.—Sp.gr. 0·978; phenols, etc., soluble in aq. $NaOH$, 44%; distils mainly between 180° and 350°C.

Blast Furnace Creosote resembles a low temperature tar, the specific gravity of the hydrocarbons being low, and little or no naphthalene being present; the proportion of phenols is high (25–35%). The phenols consist of cresols and higher homologues, and creosol and other derivatives of dihydroxy phenols are present, and the mixture has a high germicidal value. The product has a strong characteristic odour, resembling that of wood creosote. Formerly produced in large quantities in Scotland, it was employed for disinfectant manufacture and for creosoting timber. A washed oil used for benzole recovery had sp.gr.$^{15}_{15}$ 0·96; phenols 3 to 5%; distillation test, start 220°, 50% at 275°, and 70 to 75% at 300°C.; sp.heat 0·42 to 0·44 cal./g./°C. H. Moore quotes the following analysis: sp.gr.$^{20}_{4}$ 0·903, distillation start 185°, 20% 200°, 82% 225°. Calorific value gross 17,986, nett 17,286 B.Th.U. per lb.; viscosity (Redwood) 5·7 at 70°F.; phenols 23%; ultimate analysis, C 82·6, H 9·9, O+N 7·22, S 0·28%. Production has now practically ceased, metallurgical coke now replacing coal for reduction purposes.

Water Gas Tar Creosote is characterised by the absence of phenols. It is usually rich in paraffins, is of low specific gravity, and may contain naphthalene and anthracene.

F. M. P.

CRESATIN, *m*-cresyl acetate.

CRESOL, $C_6H_4(CH_3)OH$. The three isomeric cresols exist in coal tar (Williamson and Fairlie, Annalen, 1854, **92**, 319; Ihle, J. pr. Chem. [ii], **14**, 442; Tiemann and Schotten, Ber. 1878, **11**, 767, 783) in approximately the following ratio: *ortho*cresol, 35 to 40; *meta*cresol, 40; and *para*cresol, 25. The crude *carbolic acid* obtained by washing the light oil and carbolic oil fractions from the primary distillation of coal tar (*cf.* Coal Tar, Carbolic Acid) with aq. $NaOH$ and decomposing the carbolate so obtained with CO_2, contains phenol in association with the three cresols and xylenols. On fractionation in a still heated by steam coils operated under vacuum and fitted with a highly efficient column, there are obtained a phenol fraction—an intermediate fraction which on cooling yields further crude phenol and a liquid of high *ortho*cresol content—a crude *ortho*cresol—a second intermediate fraction containing a mixture of the isomeric cresols—and finally a crude *meta-para* fraction.

The two fractions of high *ortho*cresol content are refractionated, yielding technical *o*-cresol, which is further purified by fractional crystallisation. The crude *meta-para* fraction is fractionally redistilled to yield a product containing at least 50% *meta*cresol (*cf.* Cresylic Acid) or if the isomers are to be separated, a process impossible by distillation, a close-cut fraction containing 58 to 60% *meta-*, 42 to 40% *para*-cresol is collected and treated by one of the following methods.

The general method is based on the separation of the corresponding sulphonic acids. The meta-para mixture is heated to 100° with four times its weight of conc. H_2SO_4 or the mixture is treated without external heating with three times its weight of fuming sulphuric acid (20% SO_3). Sufficient water is added to the charge to reduce the boiling-point on the passage of superheated steam to 116–120°. The *meta*-cresol sulphonate hydrolyses and *m*-cresol distils over. The *para*-acid is finally decomposed by superheated steam at 140° (Raschig, B.P. 25269/1899, G.P. 114975; Brückner, Z. angew. Chem. 1928, **41**, 1043, 1062). Alternatively, Raschig proposed to separate the sulphonic acids by taking advantage of the higher solubility of the *m*-cresol derivative in sulphuric acid, the *para*-cresol sulphonic acid being allowed to crystallise out by prolonged standing, the *meta*-cresol sulphonic acid being obtained from the mother liquors (B.P. 18334/1899), or a soluble sodium salt such as the sulphate, may be added in sufficient quantity to form the sodium salt of *p*-cresol sulphonic acid, which crystallises out. The separated sulphonic acids are hydrolysed by steam. If insufficient H_2SO_4 is used, the *m*-cresol is preferentially attacked, and the unconverted *p*-cresol can be extracted by benzene (Hofmann-Laroche, F.P. 434534, *cf. also* Terrisse, G.P. 281054). Schülke and Mayr (G.P. 268780) effect preferential sulphonation of the *m*-cresol by employment of H_2SO_4 of 80 to 90% strength, and obtain a product containing 90% *m*- and 10% *p*-cresol, which is further purified by resulphonation with insufficiency of acid or by freezing (Elger, U.S.P. 1015616). In G.P. 148703, sodium hydrogen sulphate is employed as the agent preferentially sulphonating *m*-cresol.

It has also been suggested to separate the *meta*- and *para*-cresols by means of their barium salts (G.P. 53307, 152652), or their calcium salts (G.P. 152652).

Rütgers (G.P. 137584, 141421) treats the mixture of isomers with anhydrous oxalic acid or an anhydrous acid oxalate at 100°C. By this means the oxalic ester of *p*-cresol alone is formed and separates out; it is filtered off and decomposed by water into *p*-cresol and oxalic acid; the *m*-cresol is obtained from the mother liquors. According to Darzens (Compt. rend. 1931, **192**, 1657; B.P. 107961) the *p*-cresol forms complexes that are true addition compounds of 1 mol. cresol with 1 and 2 mols. respectively of oxalic acid, formed without elimination of water. Darzens separates *m*-cresol by means of the complex formed by the combination of 2 mols. *m*-cresol with 5 mols. anhydrous sodium acetate in the presence of an organic solvent. The complex is separated, washed, and decomposed with water.

Schering-Kahlbaum A.G. (B.P. 297083) effect separation by means of the urea addition compound of *m*-cresol. Desseigne (Mém. Poudres, 1934–35, **26**, 134–157) dissolves 1·1 to 1·5 mols. urea per mol. *m*-cresol in the 60:40 meta-para mixture at a temperature not exceeding 120°, adds petrol (b.p. 120–160°) with agitation, and cools to obtain the *m*-cresol compound which is separated and decomposed by water at 50°. The yield of *m*-cresol is given as 83% and the pure *para*-compound is obtained from the residues by means of the oxalic acid compound (*see also* Bentley and Catlow, B.P. 374010).

*ortho*Cresol (2-hydroxytoluene) forms colourless crystals or a white crystalline mass which discolours on exposure to light, crystallising-point 30·45° (Dawson and Mountford, J.C.S. 1918, **113**, 925); 30·75° (Bridgman Physical Rev. 1914, [2], **3**, 184); boiling-point at 760 mm. 191°C., 600 mm. 182°, 400 mm. 168°, 163 mm. 140°, 76 mm. 120°, 49 mm. 110°, (Brückner, Z. anal. Chem. 1928, **75**, 289); d_4^{20} 1·0465, d_{40}^{40} 1·0290; soluble to 3·0 vol. per cent. in water at 40°; conductivity $0{\cdot}127\times10^{-8}$ at 25°; n_D^{40} 1·5372; specific heat 0–20°, 0·499. Forms dibromo- and dinitro-derivatives. At low temperatures yields additive compounds with pyridine and naphthalene. Standard commercial grade has crystallising-point 30·3–31·0° (B.S. 522, 1938).

*meta*Cresol (3-hydroxytoluene) is normally a colourless, hygroscopic liquid when fresh, becoming slightly brown on keeping; crystallising-point 11·8° (Darzens, Compt. rend. 1931, **192**, 1657); boiling-point 760 mm. 202°, 600 mm. 193°, 305 mm. 170°, 110 mm. 140°, 48 mm. 120°, 19 mm. 100° (Darzens, *ibid.*) d_4^{20} 1·0336, d_{40}^{40} 1·0184; soluble to 2·5 vol. per cent. in water at 40°C.; conductivity $1{\cdot}397\times10^{-8}$ at 25°; n_D^{40} 1·5332, n_D^{22} 1·5352; specific heat 0–20°, 0·479; mol. heat of evaporation 10,860 cal. Forms tribromo- and trinitro-derivatives. Standard commercial grade has sp.gr.$_{15\cdot5}^{15\cdot5}$ 1·037–1·040; crystallising-point not lower than 10·5° (B.S. 522, 1938).

*para*Cresol (4-hydroxytoluene) forms hygroscopic colourless prismatic crystals which discolour on keeping; crystallising-point 36·0° (Fox and Barker, J.S.C.I. 1918, **37**, 268T); boiling-point at 760 mm. 202·3°, 500 mm. 187°, 217 mm. 160°, 106 mm. 140°, 47 mm. 120°; d_4^{20} 1·0347, d_{40}^{40} 1·0186; soluble to 2·3 vol. per cent. in water at 40°C.; n_D^{40} 1·5319 (Gibbs, J. Amer. Chem. Soc. 1927, **49**, 839). Forms dibromo- and dinitro-derivatives. At low temperatures yields additive compounds with pyridine and naphthalene. Standard commercial grade has crystallising-point not lower than 34° (B.S. 522, 1938).

For analytical methods, *see* Cresylic Acid.

Employment—The main market demand for the cresols is for mixtures of the isomers of controlled composition particularly with respect to the content of the *ortho*- or *meta*-cresols, or for the general mixture sold as cresylic acid (*q.v.*). There is, however, a growing demand for the pure isomers as raw materials for the production of derivatives required by the organic chemical industry. Some of the more important uses are as follows: *o*-cresol is used to a limited and unimportant extent in the dyestuffs industry, the ammonium and potassium salts of dinitro-*o* cresol were previously employed under the name " Victoria Yellow "; *p*-nitro-*o*-chlor-*o*-cresol is a basic material for the production of sulphur dyes and *o*-cresotinic acid is employed in manufacture of cotton and azo dyes. The use of the potassium salt of dinitro-*o*-cresol as an ingredient of plant washes has been patented; *o*-cresyl phosphate is a starting material for coumarin (Agfa, G.P. 246871, F. Raschig, G.P. 223684), and finds increasing employment as a plasticiser and fire retarder for nitro cellulose and celluloid. The resin from pure *o*-cresol and formaldehyde is odourless and has been patented as a shellac substitute.

Trinitro-*m*-cresol (*cresylite*) has been employed as an explosive. *m*-Cresol is the starting-point for Musk Ambrette and for synthetic thymol.

p-Cresyl methyl ether is employed in perfumery in the preparation of synthetic ylang-ylang oil (Schimmel A.-G., G.P. 142859, *also* Perf. & Essent. Oil Rec. 1923, **14**, 398), and the amino-derivative of this compound in the production of azo dyes. Another important derivative of *p*-cresol is anisic acid.

Under controlled oxidising conditions (copper oxide and caustic soda) the cresols yield the corresponding hydroxybenzoic acids and by the action of carbon dioxide on the sodium salts the cresotinic acids (*q.v.*) are formed.

In general, the toxicity decreases and the germicidal value of the phenol homologues increases as the alkyl group increases in complexity (Coulthard, Marshall and Pyman, J.C.S. 1930, 280). The phenol coefficient of the cresols is 2·2±0·2. A number of derivatives of *m*-cresol of high germicidal value have been prepared, *e.g.* amyl-*m*-cresol, phenol coefficient 200–300; 5-chloro-*m*-cresol, phenol coefficient in aqueous solution 133, in soap solution 24, in caustic soda solution 8 (Rapps, J.S.C.I. 1933, 52, 175T).

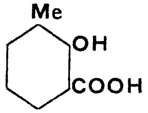
F. M. P.

CRESOL COMPOUNDS IN PERFUMERY. A number of cresol compounds have recently come into vogue as synthetic perfume materials. Of these the following are the most important: *para*cresyl methyl ether, $C_7H_7{\cdot}OMe$, has a well-defined odour of wallflowers with a definite suggestion of ylang-ylang; sp.gr. 0·978; b.p. 177°; ref. ind. 1·5123. The butyl ether is similar, but has a different " nuance." The phenyl ether, $C_7H_7{\cdot}OPh$, has a very powerful odour of the hyacinth-rose type, it has the following characters: sp.gr. about 1·063, ref. ind. 1·5720. *p*-Cresyl acetate, $C_6H_4Me{\cdot}OAc$, is a synthetic perfume having a very penetrating odour of narcissus, and is used in many perfumes of the lily, lilac and honeysuckle types, it has sp.gr. 1·055, ref. ind. 1·5025, b.p. 209°. *p*-Cresyl phenylacetate, $C_6H_5{\cdot}CH_2{\cdot}COO{\cdot}C_7H_7$, is used to a considerable extent as a narcissus perfume. It is a crystalline substance melting at 75°.

E. J. P.

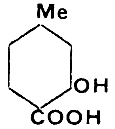
CRESOTIC ACID. The ten isomeric hydroxy-toluic acids (empirical formula, $C_8H_8O_3$) are sometimes called cresotic acids, a term which indicates their relationship with the cresols. In American terminology the name is applicable to all ten isomers, *e.g.* 4:3-cresotic acid is 4-hydroxy-3-methyl-benzoic acid. In the German system of nomenclature the name " Kresotinsäure " is restricted to the following three compounds, which are obtainable from *o*-, *m*-, and *p*-cresol respectively by the action of carbon dioxide, sometimes under pressure, in the presence of alkali (the Kolbe synthesis):

*ortho*Cresotic acid, or 2-hydroxy-*m*-toluic acid, m.p. 165°:

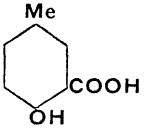


(For manufacture, *see* G.P. 138563, 624318.)

*meta*Cresotic acid, or 3-hydroxy-*p*-toluic acid, m.p. 177°:



*para*Cresotic acid, or 4-hydroxy-*m*-toluic acid, m.p. 150°:



(For manufacture, *see* G.P. 138563.)

They are homologues of salicylic acid which they resemble in general properties. Some derivatives have been reported to have medicinal value.

CRESOTINIC ACID *v.* Cresotic Acid.

CRESYL ETHER (*di-cresyl oxide*), $(C_7H_8)_2O$. There are three forms, *o*, *m*, and *p*. The di-ortho- compound boils at 275° and is used in the preparation of artificial geranium perfume.

CRESYLIC ACID. The mixture of non-crystallisable, higher boiling phenols obtained in the manufacture of carbolic acid (*q.v.*) from 60's carbolic acid is, after redistillation, known commercially as cresylic acid or liquid carbolic acid. When a good market demand exists, the creosote oil fractions distilling after the carbolic oil fraction (*v.* Coal Tar) may also be washed with caustic soda solution for the recovery of the phenol contents. (For recovery processes from ammoniacal liquor, *see* Carbolic Acid). The product is a clear liquid varying in colour from white to dark reddish or yellowish-brown, and containing 95 to 100% phenols according to grade, the chief impurities being neutral oils (naphthalene and methylnaphthalene), pyridine bases, and water. The normal refined product consists substantially of cresols and/or xylenols, and may contain phenol in relatively small amounts. Formerly cresylic acid contained *o*-, *m*-, and *p*-cresols in the proportions they occurred in the carbolic oil, *i.e.* 35:40:25, but the development of the synthetic resin (phenols-formaldehyde) industry has led to a demand for products of closely standardised *ortho*- and/or *meta*-cresol content, with the result that ordinary cresylic acid may vary somewhat widely in composition. The specific gravity may be within the limits 1·030 and 1·050, and the distillation range may lie within the limits 190° and 220°C. The acid should be sweet smelling, contain not more than traces of sulphuretted hydrogen, and react neutral to moistened litmus paper. The "British Pharmacopœia" 1932 quality has sp.gr.$^{15\cdot5}_{15\cdot5}$ 1·035–1·050; on distillation not more than 2% passes over below 188° and not less than 80% distils between 195° and 205°. The hydrocarbon content is below 0·5%, bases calculated as C_5H_5N below 0·1%, residue on evaporation below 0·1%. The acid is almost completely soluble in 50 parts of water, the solution having a pungent taste, and freely in alcohol (90%), ether, chloroform, light petroleum, glycerine, and in fixed and volatile oils. The purer grades dissolve in dilute caustic soda to give a clear solution or one from which only a few flakes of naphthalene separate on standing. B.S.S. 515, 1938, recognises five grades, the purest grade containing not more than 0·5% impurities (water, pyridine bases, and neutral oils), and the lowest grade up to 5% impurities, of which not more than 2·5% may be neutral oils. The standard cresylic acid of high *meta*cresol content is a colourless to pale straw liquid and has sp.gr. $^{15\cdot5}_{15\cdot5}$ 1·035–1·040, *meta*cresol content 50–55%, water content below 0·5%, neutral oils and bases each separately below 0·1% and distils 92% between 199° and 204°C. (*cf.* B.S. 521, 1938, and German and Japanese Pharmacopœias). The corresponding product of high *ortho*cresol content contains not less than 45% *ortho*cresol, has sp.gr.$^{15\cdot5}_{15\cdot5}$ 1·045–1·050, distils not less than 90% between 192° and 200°, and conforms to the impurity limits quoted above for the high *meta*cresol product (*cf. also* Cresols).

Cresylic acid is highly poisonous. The phenol coefficient as determined by the Rideal-Walker method lies between the limits 2 and 5, depending upon the proportion of higher phenols present. Cresylic acid from low temperature tars and some vertical tars tends to give a pink solution in alkalis, and a number of methods have been patented for overcoming this disadvantage (B.P. 397847, U.S.P. 1822842).

Methods of Analysis.—The cresols and homologues may be identified by means of the corresponding aryloxyacetic acids formed by heating the sodium salt of the phenol with chloracetic acid (Fischer, Ges. Abh. Kennt. Kohle, 1917, 2, 236; Brückner, Z. angew. Chem. 1928, **41**, 1043, 1062). A method based on the fractional hydrolysis by steam of the sulphonic acid derivatives may also be employed. The phenol mixture is well shaken with an equal part of 1·84 H_2SO_4 and then heated to 103° for 3 hours to convert the *o*-sulphonic acids into the *p*-acids which are more stable at higher temperatures. The unconverted phenols are steam distilled at 103° to 104° and finally the temperature is raised to the hydrolysing point, *m*-cresol being liberated at 116–119°, phenol at 123–126°, and *o*- and *p*-cresols at 133–136°. These last are separated by conversion into the cresoxy-acetic acids, the sodium salt of the *ortho*-isomeride being the more soluble in water. Wehuizen (Rev. trav. chim. 1918, **37**, 276) and Steinkopf and Höpner (J. pr. Chem. **1926**, [ii], **113**, 137) employ the crystalline phenylurethanes to characterise the phenols.

*ortho*Cresol is quantitatively determined by the method of Potter and Williams (J.S.C.I. 1932, **51**, 59), which is based on the property of *o*-cresol of forming a crystalline compound of definite crystallising point with cineole. A mixture of 8·40 g. of the dry sample, which must contain more than 30% *ortho*cresol, and 12·0 g. pure cineole is prepared and the approximate crystallising point determined. The mixture is then warmed to a temperature approximately 5°C. above the crystallising point until all but the last traces of crystal are melted, and the crystallising point determined by the usual method. The percentage of *o*-cresol is ascertained by reference to the following table, which is based on the use of cineole of crystallising point 1·2°C. :

o-Cresol in sample. %	Crystallising point of *o*-cresol-cineole complex. °C.
100	56·4
90	53·0
80	49·6
70	45·8
60	41·5
50	36·7
40	31·0

Precautions are necessary to ensure absence of water.

If the preliminary test shows that the *o*-cresol content is lower than 30%, the test is repeated using a mixture of equal parts of the sample and of pure *o*-cresol. The cineole and the sample tested must be quite dry. The test gives reliable results in the presence of phenol, *m*-, *p*-cresols and xylenols (J.S.C.I. 1938, **57**, 212).

*meta*Cresol is determined quantitatively by the method of Raschig (Z. angew. Chem. 1900, **13**, 759) which depends upon the formation of the trinitro derivative when *m*-cresol is treated at boiling temperature with nitric acid in excess, while the *o*- and *p*-cresols under these conditions are completely oxidised to oxalic acid. The sample should not contain more than 1% of water, 5% of phenol or 10% of xylenols. The *m*-cresol content should be between 45 and 80%; 10 g. of the sample are weighed into a 50 c.c. flask and mixed with 15 c.c. 96% sulphuric acid. After being heated for an hour at 95–100°, the contents are poured into a wide-necked litre flask and rapidly cooled under the tap with a circular motion to spread the compound over the sides of the flask. 90 c.c. of dilute nitric acid (sp.gr. 1·38–1·40) are taken in a cylinder and employed in small quantities to rinse the sulphonic acid from the small flask into the litre flask. The flask is then shaken at arms' length in a fume cupboard until the sulphonic acid is completely dissolved. Gentle agitation by swirling is continued until the reaction commences as shown by the copious evolution of brown fumes. The flask is allowed to stand for 20 minutes on a plate of insulating material and the contents are then poured into a porcelain dish containing 40 c.c. water, the flask being thoroughly rinsed out, using in all 40 c.c. water. The dish and its contents are allowed to stand 2 hours ; the solid mass of trinitro-*m*-cresol is then reduced by means of a pestle to a coarse powder and transferred completely to a tared Gooch crucible. For the transference of the remainder of the solid and the washing of the powder, a total of 100 c.c. water delivered from a fine jet wash bottle is employed. The crucible and contents are dried to constant weight at 95° to 100°C. Under these condition 1 g. of *m*-cresol yields 1·75 g. of trinitro-*m*-cresol. The powder should remain solid at the temperature of drying indicating freedom from excess xylenols ; otherwise the test should be repeated with the addition of a known weight of pure *m*-cresol to the original sample. The general conditions and, in particular, the quantity of nitric acid, must be strictly adhered to in order to prevent the development of dangerous conditions (*see* "Standard Methods for Testing Tar and its Products," 2nd ed.).

Phenol in cresylic acid is determined by Chapin's method (Ind. Eng. Chem. 1920, **12**, 771), which is based on the fact that formaldehyde quantitatively bleaches the colour developed by treating phenol with Millon's reagent (an aqueous solution of neutralised mercury nitrate), whereas the colour developed by higher phenols with the reagent remains unchanged. *See also* qualitative and quantitative tests given in article on CARBOLIC ACID.

Uses.—The total production of cresylic acid in 1935 in Great Britain was of the order of 5 million gallons, of which about 35% was exported. The U.S.A. take a special grade which on distillation yields not more than 5% phenols at 190° and not more than 75% at 215°C. ; this grade is admitted duty free, the British export figure to U.S.A. in 1935 being 789,158 gallons. Chile takes 300,000 gallons cresylic acid for employment in the froth flotation process for the concentration of minerals.

The main home markets are for :

1. Synthetic resins of the phenol-formaldehyde type—the demand is mainly for a product of *m*-cresol content standardised within ±1½% of an agreed figure, normally lying between 50 and 58%. Cresylic acid is employed in place of phenol by reason of lower cost, consistent with good electrical and chemical resistance of the resin. *ortho*Cresol tends to retard, whilst *meta*cresol assists resin formation.
2. Disinfectants.—This market absorbed 456,000 gallons in 1934. This figure includes the acid used for *lysol*, emulsifying disinfectants, which give a milky emulsion with water, and which are employed as sheep dips, veterinary fluids, or for household disinfectants, soaps, and disinfectant powders.
3. Froth flotation of minerals.
4. Synthetic tannins, tricresyl phosphate (a lacquer and varnish plasticiser and fire retarder for nitrocellulose), methyl *cyclo*-hexanol (solvent, plasticiser, and wetting agent for textiles), explosives.
5. Inhibitors in production of motor fuels (high *ortho*content preferred).
6. Lubricating oil refining by solvent methods (Chem. Met. Eng. 1935, **42**, 246 ; Oil and Gas J. 1935, **33**, (45), 86 ; **33**, (51), 16).
7. Pure cresols for manufacture of derivatives required by the dyestuffs and perfumery industries.

F. M. P.

CRESYLITE. An explosive consisting mainly of 2:4:6-trinitro*meta*cresol which has been used in France for filling projectiles. A mixture of this explosive with 40% of picric acid made by melting the two components under water has also been used for the same purpose under the name of Cresylite 60/40 or Cresylite No. 2.

Manufacture.—Trinitrocresol can be manufactured by a similar process to that used for picric acid. In order to obtain a high yield it is necessary that the cresol used should consist essentially of the meta modification, since the other isomers are largely destroyed during the nitration process with considerable loss of nitric acid.

According to Wride (Arms and Explosives, 1920, **28**, 47) 28 kg. of cresol are mixed with 120 kg. of sulphuric acid (92%) in a sulphonator and stirred for one hour, the mixture attaining a temperature of about 60°C. The sulphonated cresol is then run into a nitrating pot similar to that used for picric acid, containing 98 kg. of Chili nitrate and 170 kg. of nitric acid (38%). The whole of the sulphonated cresol is added in 4 hours. During the first quarter of an hour air agitation is employed to ensure complete mixing of the materials. At the end of the 4 hours air is again blown in for half an hour, after which about 80 litres of cold water are carefully added, air agitation still being used. After standing for about 8 hours, the mother liquid is removed and the explosive washed and dried.

Yield.—Theoretically, 100 parts of cresol should yield 225 parts of trinitrocresol, but by the above process the maximum yield is about 150% of the raw material.

Properties.—Commercial trinitrocresol is a yellow substance consisting chiefly of trinitro*meta*cresol with a small percentage of other isomers. It is considerably less soluble than picric acid in water, 1 part of the explosive dissolving in 450 parts of water at 20°C., but is readily soluble in alcohol and ether.

Pure 2:4:6-trinitrocresol melts at 109·5°C., but the melting-point of the commercial product is about 100°C. It has an acid reaction and forms salts analogous to the picrates. The trinitrocresylates, however, are not so sensitive to shock as the picrates.

Trinitrocresol is somewhat less effective than picric acid as an explosive and requires a powerful initiatory impulse to cause complete detonation.

According to Kast, aqueous suspensions of the explosive dissolve appreciable quantities of metals such as lead, iron, zinc and copper, but have no appreciable action on aluminium.

H. S.

CRISALBINE (May and Baker). Gold sodium thiosulphate, used in the treatment of pulmonary tuberculosis.

CRISTOBALITE. A native form of silica (SiO_2) crystallising in the cubic system (pseudo-cubic). It was first recognised by G. vom Rath in 1886 as regular octahedra up to 2 mm. across, associated with tridymite, in cavities in andesite from the Cerro de San Cristóbal, near Pachuca in Mexico. It has since been found in volcanic rocks in the Rhenish district, Central France and California, and in certain meteorites. The milk-white, translucent crystals are twinned and exhibit optical anomalies ; these disappear suddenly at a temperature of 175°, the crystals being then truly cubic; on cooling, the birefringence reappears. Sp.gr. 2·34, hardness 6–7, refractive index 1·49, birefringence 0·0005.

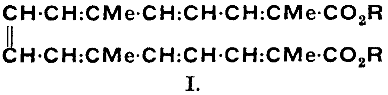
Quartz when heated passes into β-tridymite at 870°, and this in turn passes into β-cristobalite (or metacristobalite, the cubic, optically isotropic modification) at 1470°. On cooling, the latter passes into the birefringent α-cristobalite at 180–270°. The refractive index of this artificial cristobalite is about 1·484, being slightly higher than that of tridymite (1·477) ; m.p. 1710°. Cubic crystals of silica have also been obtained artificially by heating an aqueous solution of colloidal silica with hydrofluoboric acid at 200° under a pressure of 26 atmospheres. Cristobalite has also been detected in silica-bricks.

L. J. S.

CRITH. The weight of a litre of hydrogen at 0° and 760 mm. pressure—viz. 0·0898 g.

CROCEIN ACID, 2-naphthol-8-sulphonic acid. Used in making croceine scarlet and other dyes.

CROCETIN and CROCIN. Crocetin and crocin are carotenoid components of saffron (*Crocus sativus*). They are related in that crocin (I, R=gentiobiose residue), the major component of the saffron pigment, is the di-gentiobiose ester of the dicarboxylic acid crocetin (I, R=H) (Karrer and Miki, Helv. Chim. Acta, 1929, **12**, 985; Karrer and Salomon, *ibid.* 1933, **16**, 643).



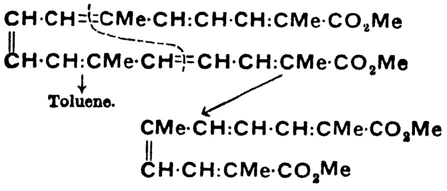
$$\begin{array}{l}\mathrm{CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CO_2R}\\ \|\\ \mathrm{CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CO_2R}\end{array}$$

I.

Crocin, $C_{44}H_{64}O_{24}$, is readily soluble in hot water but practically insoluble in alcohol or ether. On acid hydrolysis it gives crocetin and glucose, whilst with alcoholic ammonia the dicarboxylic acid is formed together with gentiobiose. Crocin is extremely sensitive to dilute aqueous potassium hydroxide giving a quantitative yield of crocetin (as potassium salt). With aqueous methyl-alcoholic alkali, however, an extraordinarily facile esterification of the crocetin occurs with formation of the mono- and di-methyl esters.

Crocetin, $C_{20}H_{24}O_4$, is insoluble in water and in most organic solvents with the exception of pyridine, from which it separates in red coloured leaves, m.p. 275–276°, which exhibit absorption maxima at 463 and 434·5 mμ in chloroform ; the potassium and sodium salts are yellow in colour.

Crocetin monomethyl ester, m.p. 218°, separates as reddish-yellow plates from chloroform-methyl alcohol. Two stereoisomeric dimethyl esters of crocetin are known, the labile *cis*-isomer, m.p. 141°, being converted into the stable *trans*- form, m.p. 242°, on exposure to light. The latter separates from chloroform-methyl alcohol in orange-red plates and exhibits optical maxima at 463 and 434·5 mμ in chloroform. On thermal degradation it yields 2:6-dimethylnaphthalene, toluene, *m*-xylene together with the dimethyl ester of 1:4:8-trimethyloctatetraene 1:8-dicarboxylic acid (II), which is formed by the remarkable transformation illustrated below:


CH·CH=C:CMe·CH:CH·CH:CMe·CO₂Me
CH·CH:CMe·CH=C=CH·CH:CMe·CO₂Me
Toluene.
CMe·CH:CH·CH:CMe·CO₂Me
CH·CH:CMe·CO₂Me

II.

The Structure of Crocetin.—Titration with alkali shows that crocetin is a dicarboxylic acid; on catalytic hydrogenation, crocetin dimethyl ester absorbs the equivalent of 7 mols. of hydrogen (Karrer and Salomon, Helv. Chim. Acta, 1927, **10**, 397; 1928, **11**, 513), from which it follows that crocetin is acyclic.

Since oxidation with chromic acid proves the presence of 4 extracyclic methyl groups, the 7 ethylenic linkages must be disposed between 14 carbon atoms. On this evidence a satisfactory formulation (I) for crocetin was advanced. This structure, and especially the location of the methyl group side chains, has been confirmed by the synthesis of perhydrocrocetin (Karrer, Benz and Stoll, Helv. Chim. Acta, 1933, **16**, 297).

Again the degradation of perhydrocrocetin to the diketone, $C_{18}H_{34}O_2$ (III):

$$HO_2C{\cdot}CHMe{-}X{-}CHMe{\cdot}CO_2H$$
$$\Big\downarrow \text{Br; KOH}$$
$$HO_2C{\cdot}CMe(HO){\cdot}X{\cdot}CMe(OH)CO_2H$$
$$\text{MeMgI} \Big\downarrow \text{on acid chloride}$$
$$HO{\cdot}Me_2C{\cdot}CMe(OH){\cdot}X{\cdot}CMe(OH){\cdot}CMe_2{\cdot}OH$$
$$\Big\downarrow Pb(OAc)_4$$
$$Me{\cdot}CO{-}X{-}CO{\cdot}Me$$

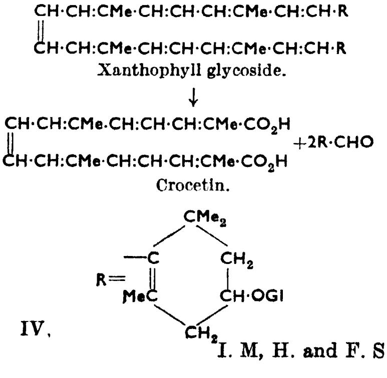
III.

and the synthesis of this diketone (6:11-dimethylhexadecane-2:15-dione) (Karrer and Lee, Helv. Chim. Acta, 1934, **17**, 545) afford a further confirmation of the correctness of the structure allocated to crocetin:

$$EtO_2C{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{\text{Na; EtOH}} OH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$
$$\xrightarrow{\text{Na; EtI}} EtO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$
$$\xrightarrow{\text{PBr}_3\text{; Na}} CH_2(OEt){\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_4{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$$
$$\xrightarrow[\text{(hydrol)}]{\text{HBr; CHNa(CO}_2\text{Et)}_2} HO_2C{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_4{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CO_2H$$
$$\xrightarrow[\text{acid chloride}]{\text{MeZnI on}} Me{\cdot}CO{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_4{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CO{\cdot}Me$$

III.

In addition to crocin, crocetin, carotene, lycopene, and zeaxanthin, saffron also contains a colourless glycoside, picrocrocin (IV), the presence of which led Kuhn and Winterstein (Ber. 1934, **67**, [B], 344) to suggest that crocetin is evolved by a phyto-chemical oxidation of a xanthophyll according to the following scheme:


CH·CH:CMe·CH:CH·CH:CMe·CH:CH·R
CH·CH:CMe·CH:CH·CH:CMe·CH:CH·R
Xanthophyll glycoside.
CH·CH:CMe·CH:CH·CH:CMe·CO₂H
+2R·CHO
CH·CH:CMe·CH:CH·CH:CMe·CO₂H
Crocetin.
CMe₂
C
CH₂
R=
MeC
CH·OGl
CH₂

IV.

I. M, H. and F. S. S.

CROCIDOLITE. (Ger. *Krokydolith.*) A mineral of the soda-amphibole group, consisting of sodium and iron (ferric and ferrous) silicate, $NaFe'''(SiO_3)_2{\cdot}Fe''SiO_3$. It is known only in a finely fibrous form, its name, in fact, being from κροκύς, κροκύδος, wool. In the trade it is known as *blue asbestos*, and it is worked for the same purposes as the other varieties of asbestos (*q.v.*). It is, however, more readily fusible (to a black magnetic glass) than are tremolite-asbestos and serpentine-asbestos. The mineral has been long known from the Asbestos Mountains near the Orange River in Griqualand West, South Africa, where it occurs abundantly as veins, 1 or 2 inches in thickness, in jasper-schists. The closely aggregated parallel fibres are arranged perpendicularly or nearly so to the walls of the veins; and the material is extracted as slabs. It is now extensively mined for commercial purposes (A. L. Hall, Asbestos in the Union of South Africa, Mem. Geol. Survey South Africa, 2nd ed., 1930, no. 12; M. A. Peacock, Amer. Min. 1928, **13**, 241).

Being an alkali silicate with ferrous iron, crocidolite is especially liable to decomposition when exposed to weathering; sodium is removed, and the iron oxidised and hydrated to form limonite, while the silica is set free. There then results a ferruginous quartz possessing the finely fibrous structure of the original mineral; or, in other words, a pseudomorph of quartz and limonite after crocidolite. This material is coloured a rich golden yellow, and displays a silky lustre, and being at the same time very hard, it is well adapted for ornamental purposes. When cut and polished with a convex surface, it displays a cat's-eye effect, and it is extensively used for making knobs, umbrella handles, beads, etc. Such material is known as *tiger's-eye*, though, unfortunately, in the trade the name crocidolite is very frequently misapplied to it. The name *pseudo-crocidolite* would be more appropriate. In some stones there has been silicification without oxidation, and the indigo-blue colour of the original crocidolite has been preserved: material of this kind is known as *hawk's-eye*. The stones are sometimes stained artificially with dyes. *See also* ASBESTOS.

L. J. S.

CROCIN *v.* CROCETIN.

CROCOITE or CROCOISITE. Lead chromate, $PbCrO_4$, crystallising in the monoclinic system. The name was originally given in the French form crocoise by F. S. Beudant in 1832, from κρόκος, saffron; this was later changed to crocoisite, and afterwards to the more correct form crocoite. This mineral is the only chromate of any importance found in nature, and in it the element chromium was discovered. It is found usually as crystals which are bright hyacinth-red in colour with a brilliant lustre; the streak is orange-yellow. On exposure to light the crystals soon deteriorate in translucency and brilliancy. Sp.gr. 6·0, hardness 2½–3. Crocoite is a mineral of secondary origin in veins of lead ore and is often associated with gold. It is found at Beresovsk in the Urals (where it was discovered in 1766), Congonhas do Campo near Ouro Preto in Brazil, Luzon in the Philippines, Umtali in Rhodesia, and as very fine crystals at Dundas in Tasmania. The mineral has been used as a pigment, being identical in composition with the artificial product chrome yellow.

L. J. S.

CROCUS OF ANTIMONY *v.* ANTIMONY OXYSULPHIDE.

CRONSTEDTITE, $H_8Fe'_4Fe'''_4Si_3O_{20}$, a variety of thuringite.

CROOKESITE. A selenide of copper, thallium (Tl 16–18%) and silver forming compact masses with lead-grey colour and metallic lustre. Sp.gr. 6·9, hardness 2½–3. It occurs embedded in calcite in the Skrikerum mine, Småland, Sweden. Although a rare mineral, it is of interest in being one of the few minerals containing thallium in considerable quantity. It was named in 1866 in honour of Sir William Crookes (1832–1919), the discoverer of thallium.

L. J. S.

CROPS. The composition of crops is usually expressed in terms of a conventional series of analyses, which, though they do not necessarily pick out sharply any particular plant constituent, are widely used for comparative purposes. Many crops are grown directly or indirectly as feed for livestock. Virtually all the quantitative information on digestibility and nutritive values is based on the same analyses, which are also used in the proper balancing of rations. For such practical purposes the figures are sufficiently precise and are unlikely to be supplanted by any other system. For research purposes, however, the use of this system of analyses is unwise, as misleading results are apt to be obtained. The analyses commonly carried out are as follow (*see* Ministry of Agriculture, Fertilisers and Feeding Stuffs Regulations, 1932, No. 658).

1. *Dry Matter.*—A weighed quantity of the sample is dried at 100°.

2. *Ether-soluble Substance* (expressed often as crude fat or oil).—The material is treated in a Soxhlet extractor with ether or light petroleum for 3–4 hours, and if necessary dried, ground finely with sand, and re-extracted for a further period of 1 hour. The solvent is evaporated and the oil dried at 100°.

3. *Crude Protein* (total nitrogen×6·25).—Total nitrogen is determined by some modification of the Kjeldahl method.

4. *Crude Fibre.*—About 2 g. of the dry material, previously extracted with light petroleum, is placed in a conical litre flask, 200 ml. of hot 1·25% sulphuric acid is added and brought to the boil within 1 minute. Boiling is continued gently for exactly 30 minutes, the original volume being maintained and the flask being rotated every few minutes. The contents of the flask are then poured into hot water in a Buchner funnel in which a filter paper is supported by a piece of cotton cloth. Filtration must be effected within 10 minutes. The residue is washed free from acid with hot water, and washed back into the conical flask with 200 ml. of hot 1·25% sodium hydroxide. The contents of the flask are again boiled gently for 30 minutes and filtered through filter paper or cloth. The residue is washed thoroughly with hot water and dilute acid, and again with water till free from acid. It may then be transferred to an ashless filter paper after further washing with alcohol and ether, and dried to constant weight. The ash may be determined by incineration and deducted from the weight of the fibre. This correction is often omitted.

5. *Ash.*—The ash content is determined by incineration at a dull red heat preferably in a muffle furnace.

The sum of the analyses, ash, crude fibre, crude protein, and ether-soluble constituents is commonly far from 100, and the difference is accordingly taken and described as "soluble carbohydrates" or "nitrogen-free extractives." This fraction frequently amounts to 50% or more of the material. A partition of the nitrogenous constituents is sometimes introduced, "true protein" or "pure protein" being that fraction precipitated by a protein precipitant such as copper acetate or metaphosphoric acid. The difference between crude protein and true protein is sometimes expressed as "amides."

Analyses of some of the principal crops, other than cereals (*q.v.*), grown in Great Britain are given in Table I. It should be emphasised that the composition may vary considerably according to age, variety, season, and soil conditions.

TABLE I.

PROXIMATE COMPOSITION OF CROPS.[1]

Crop.	Dry matter.	Ether-soluble.	Crude protein.	Crude fibre.	Soluble carbo-hydrates.	Ash.
Root Crops—						
Potatoes	25·0	0·1	2·1	0·7	21·0	1·1
Mangolds	12·5	0·1	1·3	1·0	8·9	1·1
Sugar beet	23·4	0·1	1·1	1·1	20·4	0·7
Swedes	12·2	0·2	1·5	1·3	8·2	0·9
Turnips	9·2	0·2	1·2	1·1	5·9	0·8
Carrots	13·2	0·3	1·2	1·5	9·2	1·0
Parsnips	15·0	0·3	1·3	1·2	11·3	0·9
Potato haulms	23·0	1·0	2·5	6·2	10·2	3·1
Mangold leaves	11·0	0·4	2·4	1·6	4·6	2·0
Sugar beet tops	16·2	0·5	2·0	1·6	8·7	3·4
Turnip leaves	11·6	0·5	2·2	1·5	5·3	2·1
Legumes—						
Clover (green)	18·5	0·8	4·4	4·3	6·9	2·1
Lucerne (green)	24·0	0·4	4·1	7·2	9·9	2·4
Sainfoin (green)	20·0	0·6	3·5	6·9	7·8	1·2
Tares (green).	17·5	0·5	3·2	5·1	7·2	1·5
Field beans (grain)	86·5	1·7	25·3	8·1	48·3	3·1
Field beans (straw)	81·6	1·1	8·1	36·0	31·0	5·4
Field peas (grain)	86·1	1·9	23·1	5·7	52·7	2·7
Field peas (straw)	86·3	1·6	9·0	35·5	33·7	6·6
Soya beans (grain)	89·2	16·9	33·9	4·8	28·9	4·7
Soya hay	91·6	3·8	15·8	24·3	38·8	8·9
Clover hay	83·5	2·9	13·5	24·0	37·1	6·0
Lucerne hay	83·5	2·6	14·2	29·5	29·2	8·0
Sainfoin hay	83·5	2·5	13·2	28·0	32·5	7·3
Other Crops—						
Kale, thousand-head	15·8	0·4	2·2	3·1	8·4	1·7
Kale, marrow-stem	14·0	0·5	2·2	2·5	6·9	1·9
Mustard	14·9	0·4	2·9	2·9	7·3	1·4
Cabbage	11·0	0·4	1·5	2·0	5·9	1·2
Grasses—						
Rye grass (perennial)	24·8	0·7	2·9	7·1	11·5	2·6
Pasture grass	20·0	1·1	5·3	2·6	8·9	2·1
Meadow hay	85·7	2·5	9·7	26·3	41·0	6·2
Meadow hay (aftermath) . . .	85·2	3·4	11·5	22·5	39·3	8·5

This system of analysis is more satisfactory when applied to root crops than to mature materials such as hay. The carbohydrate constituents appear in the two groups "crude fibre" and "soluble carbohydrates," the latter consisting of any non-nitrogenous material which is soluble in or hydrolysed by hot 1·25% alkali and acid. The crude fibre residue is composed almost exclusively of cellulose, but even so only represents 70–80% of the cellulose of the tissue. It may be accompanied by a small but variable proportion of the lignin. The major part of the lignin passes into solution in the hot dilute alkali and is therefore included as a "soluble carbohydrate." For this reason analyses of a maturing material do not reveal the extent of the changes undergone on lignification, since the "crude fibre" figure only increases in proportion to the increase in cellulose, and contains no estimate of the lignin which may so profoundly affect digestibility. While the "soluble carbohydrate" fraction of root crops and starchy grains is more or less accurately so described, that of maturer materials is misleading in that it includes lignin and polyuronide hemicelluloses which are structural constituents associated with the "fibre."

The nitrogenous constituents commonly expressed as crude protein are not all in that condition, and frequently only 60–80% may be precipitated by protein precipitants. The remainder may occur in a number of simpler forms such as peptones, amino-acids, amides, and even nitrate in small amounts. Asparagine has been found in a number of plants and is believed to play an important part in metabolism. The magnitude of the error caused by calculation of the total nitrogen as crude protein is not great.

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[1] Some analyses have been taken from "Rations for Livestock," Min. of Agric. Bull. 48.

Root Crops.—The chief differences between the various roots are in the nature and proportions of the carbohydrate reserves stored therein. In potatoes the characteristic carbohydrate is, of course, starch, which is deposited in the cells as granules with a banded structure. Approximations to the starch content of potatoes may be made from the specific gravity of the tuber. The amount usually stated to be present is in the neighbourhood of 20% of the fresh weight, though direct determinations of starch usually give a slightly lower figure of 70–75% on the dry weight. A small amount of sugar may also be present normally, and this may be increased if the potatoes have been subjected to a low temperature in storage. In sugar beet, mangolds, swedes and turnips the chief simple carbohydrate is sucrose, stored in the root, the amounts usually found descending in the order named. The concentration of sucrose in the sugar beet is very high, though variable. An average figure appears to be about 18% of the fresh weight. Concentrations as high as 21–22% have been found. The sucrose is always accompanied by a certain amount of reducing sugar. Traces of raffinose may be present and may accumulate in beet sugar molasses (*v.* Beet).

The leaves of the sugar beet are lower in sucrose than the root but may contain much higher amounts of reducing sugars. Analysis of the whole plant, and leaves and roots separately have been given by Knowles, Watkin, and Hendry, J. Agric. Sci. 1934, **24**, 368:

	Whole plant.	Leaves.	Roots.
Dry matter	20·26	14·21	25·10
On dry basis.			
Ash	8·60	21·00	2·99
Total sugars as sucrose	53·68	14·57	71·40
Sucrose	48·95	3·23	69·63
Reducing sugars	4·73	11·34	1·77

Mangolds also contain considerable quantities of sucrose, but not at such a high concentration, 6–8% sucrose is commonly found. The dry matter of mangolds (10–13%) is much lower than that of sugar beet, so that on the basis of dry matter the difference between sugar beet and mangolds is not great. The yield of mangold roots per acre is more than twice that of sugar beet, but nevertheless, the sugar beet as the more concentrated source has the advantage. The leaf/root ratios of these two crops are entirely different. One part of top makes on the average 0·75 parts of root of the sugar beet, and 5 parts of root of mangolds. Swedes and turnips contain less sucrose, 4–5% having been recorded.

It should be mentioned that the cell-wall of these roots contains pectin in amounts higher than is met with in most other tissues except certain fruits. Pectin from the sugar beet particularly has been the subject of investigation by Ehrlich (Ehrlich and von Sommerfeld, Biochem. Z. 1926, **168**, 263; Ehrlich and Schubert, Ber. 1929, **62**, [B], 1974). The nitrogenous constituents of root crops have not been extensively investigated, the most recent report being that of Davies on mangolds (J. Agric. Sci. 1926, **16**, 293).

Legumes.—The importance of leguminous crops lies in their high protein content, and in a number of cases the proteins have been fractionated and constituent amino-acids determined (*v.* Osborne and collaborators, J. Amer. Chem. Soc. 1890–1903, and later in J. Biol. Chem.; *also* Davies, J. Agric. Sci. 1926, **16**, 280). Detailed analyses have been made of lucerne at various stages of growth and intervals of cutting (Graber, Wis. Agric. Expt. Sta. Res. Bull. 80, 1927). Separate analyses of leaf and stem have been carried out by Woodman (Woodman and Eden, J. Agric. Sci. 1935, **25**, 578) and expressed on the dry basis:

	Young leaf.	Young stem.	Mature leaf.	Mature stem.
Ash	12·26	9·78	13·94	7·03
Ether-soluble	3·43	1·20	3·01	1·03
Crude protein	30·13	16·97	23·48	9·44
Crude fibre	12·99	30·77	13·39	44·36
Soluble carbohydrates	41·19	41·28	46·18	38·14

The nature of the fraction described as soluble carbohydrates has not been examined, but it is probably composed to a considerable extent of hemicelluloses and lignin together with about 10% starch. The leguminous seeds also contain starch, the granules being of characteristic size and shape. Soya beans are unusual in containing up to 20% oil, which has found commercial uses. The ash of leguminous plants (other than seeds) is usually distinctly high in calcium, as will be seen in Table II.

Other Crops.—Because of its increasing use as a winter feed kale has been the subject of investigation by Woodman (Woodman, Evans and Eden, J. Agric. Sci. 1936, **26**, 212). The compositions of the two leading varieties, marrow-stem and thousand-head, are very similar:

	Marrow-stem.	Thousand-head.
Ash	11·49	11·27
Ether-soluble	2·81	2·56
Crude protein	14·64	15·81
Crude fibre	18·34	21·29
Soluble carbohydrates	52·72	49·07

Separate analyses of the leaf, marrow, and rind have been made in the case of marrow-stem kale:

	Leaf.	Marrow.	Rind.
Ash	14·86	15·19	7·05
Ether-soluble	3·33	1·34	0·81
Crude protein	13·87	12·03	7·72
Crude fibre	12·45	13·06	29·08
Soluble carbohydrates	55·49	58·38	55·34

The marrow of the kale stem is rich in sugar, the major part being in the form of reducing sugars, not as sucrose:

	Marrow-stem kale.		Thousand-head kale.	
	Oct. 14.	Jan. 24.	Nov. 20.	Feb. 14.
Total sugars	54·37	45·53	47·57	43·91
Reducing sugars	50·32	21·85	29·90	29·24
Sucrose	4·05	23·68	17·67	14·67

Grasses.—The composition of grass varies widely according to the species, age and manurial conditions. Young spring growth is higher in protein than summer growth, unless nitrogenous fertilisers are applied. Aftermath may generally be taken as containing more fibre than spring growth of a similar nitrogen content. Analyses of the nitrogenous constituents of grasses have been made by Chibnall and Miller, J. Biol. Chem. 1931, **90**, 189; Greenhill, Biochem. J. 1936, **30**, 412). The latter found the proportion of the total nitrogen present as true protein to be more or less steady in intensively grazed pasture grass, the value being usually between 85% and 90% and rarely below 80%. Abnormally high proportions of non-protein nitrogen have occasionally been observed and have been believed to be the cause of digestive disturbances in stock.

The figure for soluble carbohydrates in grasses and hays is commonly 40–50%, but this is due largely to the deficiencies of the system of analysis, as mentioned earlier. Small amounts of fructosans have been reported in grasses, and amounts up to 30% have been found in young rye grass, disappearing as maturity is approached (Norman, Biochem. J. 1936, **30**, 1354). Detailed analyses of many grasses have been made by Fagan (Welsh Plant Breeding Station, Bull. Series H, No. 3, 1924; No. 9, 1926–27), by Woodman, and by S. J. Watson (J. Agric. Sci. 1928–1936).

Ash of Crops.—The mineral constituents of crops have acquired a new importance in view of advances in animal nutrition and the recognition of the rôle of minor elements in development and maintenance of condition. Aspects of this question are dealt with by Sir John Orr ("Minerals in Pastures," 1929). The composition of the ash was originally studied as a result of the view that the fertiliser requirements of the plant could best be determined by a knowledge of the constituents taken away from the soil by that particular crop. Some ash analyses are given in Table II.

Table II.

Composition of the Ash of some Crops.

	Ash on dry basis.	As % of ash.						
		CaO	K_2O	Na_2O	MgO	P_2O_5	Cl	SiO_2
Potatoes	3·99	1·53	58·27	0·06	3·48	12·86	7·27	0·58
Mangolds	6·70	3·58	35·90	19·34	2·13	9·34	3·87	0·97
Sugar beet	2·99	15·39	27·42	—	—	18·40	4·02	4·02
Swedes	5·58	12·12	39·17	5·24	3·02	9·83	2·48	0·72
Clover	8·15	37·37	13·10	0·58	5·10	3·75	2·26	0·54
Lucerne (leaf)	13·94	40·10	15·35	0·50	—	4·52	3·59	0·86
Lucerne (stem)	7·03	25·46	33·01	0·57	—	6·69	5·12	1·28
Beans (grain)	3·27	5·60	40·58	2·12	6·61	30·69	2·43	0·41
Beans (straw)	5·80	28·39	8·07	14·57	3·12	2·31	2·49	3·08
Peas (grain)	2·53	5·74	44·31	0·39	8·97	29·30	0·45	0·37
Peas (straw)	5·87	40·34	11·78	9·90	8·30	8·26	3·84	10·66
Lucerne hay								
Kale, thousand-head	11·27	21·22	34·44	1·24	3·91	8·78	9·85	0·27
Kale, marrow-stem	11·49	21·32	33·85	2·26	3·39	7·83	11·23	0·87
Rye grass	9·59	8·02	—	—	—	6·77	6·77	45·45
Pasture grass	9·03	8·71	35·40	5·13	—	8·64	9·62	21·70

Other Methods of Analysis.—The system of analyses of organic constituents described above is official in the sense that the evaluation of feeding-stuffs is based upon it. There is, however, a distinct movement towards analyses which determine as closely as possible each important constituent instead of indefinite fractions. A proximate system was proposed by Waksman and Stevens (Ind. Eng. Chem. [Anal.], 1930, 2, 167), which, while not perfect, is a considerable advance. This procedure tends to over-estimate the hemicelluloses at the expense of the cellulose. Examples of analyses by this system are given in Table III.

Table III.

Proximate Composition of Some Plant Materials (Waksman and Stevens).

	Maize stalks.	Lucerne.	Timothy hay.	Oak leaves.
Ether and alcohol soluble fraction	3·42	10·41	2·90	9·93
Hot water soluble fraction	28·27	17·24	16·92	10·26
Hemicelluloses	20·38	8·52	22·07	15·62
Cellulose	23·05	26·71	26·09	17·18
Lignin	9·68	10·78	16·21	29·66
Crude protein	2·61	8·13	3·25	3·47
Ash	7·40	10·30	5·68	4·68

Figures for cellulose and lignin contents would frequently be of value in considering the composition of crops and particularly in following developmental changes which are very imperfectly reflected in simple crude fibre determinations. Detailed studies of this nature have been carried out on a variety of materials (Norman J. Agric. Sci. 1933, **23**, 216; Buston, Biochem. J. 1934, **28**, 1028; Phillips and Goss, J. Agric. Res. 1935, **51**, 301; Norman, Biochem. J. 1936, **30**, 1354). Although, of the structural constituents, cellulose and lignin may be determined with some degree of accuracy, the same cannot yet be said of the hemicelluloses. A laborious procedure of direct extraction and weighing has been suggested (Preece, Biochem. J. 1931, **25**, 1304), and used on grasses and leaves (Buston, Biochem. J. 1935, **29**, 196), but a more expeditious and accurate method of determining this important group of polysaccharides is required.

A. G. N.

CROTALINÆ *v.* Blood Anticoagulants.

CROTINE *v.* Croton Oil.

CROTON OIL (*Oleum crotonis, Oleum tiglii* of the Pharmacopœias; Fr. *huile de petits pignons d'Inde*) is obtained from the seeds of the shrub or small tree *Croton Tiglium* L. (Fam. Euphorbiaceæ), which is indigenous to S. India and Ceylon but found in cultivation in other tropical regions of S. Asia and Oceania.

The oil, which amounts to about 30–45% of the whole seed (equivalent to 43–63% of the kernel) is recovered commercially by expression or by extraction with solvents (alcohol, ether, etc.) from the shelled or unshelled seeds according to the requirements of the various national Pharmacopœias[1]: the colour of the oil, its physiological activity, and its solubility in alcohol (which depends chiefly on the content of free fatty acids) depend on the method employed for its extraction.

Both seeds and oil should be handled with extreme caution, as they not only possess dangerous toxic and purgative properties when taken internally, but also display a serious vesicating action when applied externally to the skin (distinction from Curcas Oil, *q.v.*). (According to Cherbuliez, the purgative effect may also follow the application of the oil to the skin.)

In addition to the vesicant and purgative principles, which pass into the expressed or extracted oil, the seed kernels also contain two toxalbumins—**crotonglobulin** and **crotonalbumin**—(which were formerly classed together under the name "crotine" (*see* Stillmark, Arb. Pharmak. Inst. Dorpat, 1889; Elfstrand, Habil.-schrift, Upsala, 1898; Kobert, Landw. Versuchs-Stat. 1913, **79–80**, 97)), sucrose and glycose glycosides, and about 1–4% of a glycoside, **crotonoside**, which has been identified as the *d*-riboside of 2-hydroxy-6-amino-purine (*iso*guanine), and which (in small doses at least) has no harmful physiological action (Cherbuliez and Bernhard, Helv. Chim. Acta, 1932, **15**, 464, 855, 978).

Croton oil is used to a limited extent as a drastic cathartic (usually in admixture with castor oil or other diluent), and more frequently as a constituent of rubefiant liniments, etc., in cases of pneumonia, sciatica, etc.

The vesicating action of the seeds and oil is associated with an amorphous material, termed "Naturgiftstoff" by Flaschenträger (Böhm and Flaschenträger, Arch. exp. Path. Pharm. 1930, **157**, 115; *l.c., infra*) and "Résine de croton" by Cherbuliez, Ehninger, and Bernhard (Helv. Chim. Acta, 1932, **15**, 658), which can be extracted by purely physical methods (extraction with methanol) from croton oil, or in somewhat higher yield (*c.* 1–3%) from the seeds themselves. This material varies in its properties according to the manipulation employed for its recovery, and appears to consist of a complex mixed unsaturated ester (or mixture of esters) containing some free hydroxyl (phenolic ?) groups: it is extremely sensitive to alcoholysis, especially in the presence of alkalis, and it is almost certain that the glassy, toxic **croton resin**, recovered by even such mild methods as were used by Dunstan and Boole (Proc. Roy. Soc. 1895, **58**, 238), Böhm (1915, *l.c., infra*), and other early investigators represented a product of the partial decomposition or modification of the original natural toxin. Croton resin, like the "Naturgiftstoff" from which it is derived, displays the toxic and vesicating properties of the oil to an enhanced degree, but is very easily saponified by alkalis (*see* Dunstan and Boole, *l.c.*; Flaschenträger, G.P. 638004, and *l.c., infra*[2]), yielding a complex mixture of physiologically inactive products; these include a crystalline tricyclic phenolic compound, **phorbol** ($C_{20}H_{28}O_6$?), containing five hydroxyl groups and three unsaturated linkings, and about 32–35% of a complicated mixture of fatty acids, among which formic, acetic, *iso*butyric, tiglic, caprylic, capric, lauric, myristic, palmitic, oleic and linolic acids have been identified (Böhm, Arch. exp. Path. Pharm. 1915, **79**, 138; Spies, J. Amer. Chem. Soc. 1935, **57**, 180; J. Org. Chem. 1937, **2**, 62); higher saturated acids and more unsaturated acids appear to be absent.

Little is known concerning the cause of the purgative action of the oil, which would appear to be attributable to some factor other than the croton resin, since Cherbuliez finds that croton oil, from which the bulk of the toxic resin has been extracted, still retains its cathartic activity. The "crotonoleic" acid of Buchheim (Wagners Arch. Heilk. 1872, **13**, 1, 20; 1873, **14**, 1), and of Kobert (Chem.-Ztg. 1890, **14**, 656) has been shown by Dunstan and Boole to have been an impure mixture of croton resin and fatty acids. Both croton oil and croton resin lose their specific physiological action upon hydrogenation.

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[1] Descriptions of *Oleum crotonis* (*Oleum Tiglii*), which appeared in former editions have been omitted from the most recent revisions of the British (1932), United States (1936), and Dutch (1926) Pharmacopœias; liniments containing croton oil still appear in the B.P.C.

[2] Phorbol and the product of its benzoylation are physiologically inactive, but the (? tetra-)acetate is highly toxic; on treatment with sulphuric acid, phorbol yields the ketone **crotophorbolone**, $C_{20}H_{26}O_5$, (Flaschenträger and von Falkenhausen, Annalen, 1934, **514**, 252; Böhm, Flaschenträger, and Lendle, Arch. exp. Path. Pharm. 1935, **177**, 212; on further alkaline hydrolysis of phorbol, phenolic (enolic) derivatives are obtained.

The following analysis of croton oil by Flaschenträger and von Wolffersdorff (Helv. Chim. Acta, 1934, **17**, 1444; *cf.* Schmidt and Berendes, Annalen, 1877, **191**, 94) indicates roughly the quantitative composition of the oil (the "percentages" are only approximate, since the item of "loss" amounts nearly to 14%): "Naturgiftstoff" (toxic resin) 3·4% (the combined acids present in this fraction are not included in the subsequent figures); oleic acid 37%; linolic acid, 19%; arachidic acid, 1·5%; stearic acid, 0·3%; palmitic acid, 0·9%; myristic acid, 7·5%; lauric, tiglic, valeric and butyric acids, each in traces less than 0·05%; acetic acid, 0·6%; formic acid, 0·8%; acids insoluble in light petroleum 6·9%; "undetermined acids," 0·6%; glycerol, 7·2%; unsaponifiable matter (including a sterol, m.p. 131°C.) 0·25%; loss 13·8%. As the whole of the "Naturgiftstoff" was not removed from the oil by the method employed, the results of the analysis are not inconsistent with the opinion of Böhm that all the lower (volatile) fatty acids, including the stable solid, unsaturated **tiglic** acid ($CH_3{\cdot}CH{:}C(CH_3){\cdot}COOH$; m.p. 64·5°C., isomeric with angelic acid), are associated with the vesicant principle, and do not form any part of the glycerides constituting the true fatty oil of the seed. Adriaens (Congo, Dec. 1934) reports 89–90% of insoluble fatty acids in croton oil, of which 9·5–10·5% are stated to consist of saturated, and 89·5–90·5% of unsaturated acids. As much as 0·6% of tiglic acid has been isolated from crude croton oil (Geuther and Fröhlich, Z. Chem. 1870, N.F. **6**, 549, 576).

Croton oil is strongly dextrorotatory, $[a]_D^{c.\ 20}$ +5° to +9°; owing to its remarkable composition, which differs widely from that of all other oils, its recognition by means of the ordinary quantitative reactions is not difficult: the following figures illustrate the usual ranges: m.p. −7° to −16°C., sp.gr.^{15} 0·9320–0·9501; n_D^{20} 1·4734–1·481; acid val. 2–55; saponification value 200–215; iodine value (Wijs) 102–115; Reichert-Meissl value 12–13·6 (Lewkowitsch), 6·4–8·4 (Adriaens); Polenske value 1·3 (Adriaens); true acetyl value 19·8–32·7 (Lewkowitsch), 5·6–11 (Adriaens). In admixture with other vegetable oils, croton oil may be detected by the characteristic reddish ring which appears at the junction of the liquids when a solution of the oil in two volumes of absolute alcohol is poured on to a concentrated solution of potassium or sodium hydroxide (Comte, J. Pharm. Chim. 1916, [vii], **14**, 38; the reaction is due to the toxic resin).

The oil obtained from the seeds of an allied E. African plant, *Croton megalocarpus* Hutch (=*C. Elliottianus* Pax and Eng.),[1] and known in pharmacy as *Oleum crotonis Elliottianus* or *Ol. Elliott.*, has a comparatively non-irritant purgative action, and does not appear to contain any vesicating constituent; the characteristics of the oil, viz. sp.gr.^{15} 0·925–0·927, saponification value 188·5–201·5, iodine value 138·6–147·5, insoluble fatty acids 94–94·8%—also differ considerably from those of croton oil (*cf.* Bull. Imp. Inst. 1907, **5**, 237; 1915, **13**, 39; 1923, **21**, 206; Cash and Dilling, J. Pharm. Exp. Therap. 1914, **6**, 235; Martindale and Westcott, Extra-Pharmacopœia).

E. L.

CROTON RESIN *v.* Croton Oil.

CROTONALBUMIN *v.* Croton Oil.

CROTONGLOBULIN *v.* Croton Oil.

CROTONITRILE *v.* Allyl.

CROTONOLEIC ACID *v.* Croton Oil.

CROTONOSIDE *v.* Croton Oil.

CROTONYLENE *v.* Acetylenes.

CROTOPHORBOLONE *v.* Croton Oil.

CROWBERRY (*Empetrum nigrum*). The leaves of the crowberry contain a wax composed of ceryl cerotate, benzoic acid, ursone, tannin, dextrose, and probably rutin. The anhydrous ursone, $C_{10}H_{16}O$, is identical with that obtained from the leaves of *Uva Ursi*. *Empetrum nigrum* contains no alkaloids or andromedotoxins or glucosides decomposed by emulsin (van Itallie, Pharm. Weekblad, 1918, **55**, 709).

CRUCIBLES. Crucibles may be described as hollow vessels constructed of material which can resist the action of heat and chemical attack and possess mechanical strength at high temperatures. This description takes no account of size and thus embraces types ranging from small laboratory utensils to industrial plant; and crucibles which will give satisfactory results in service are some of the most difficult refractory articles to produce. The requirements of a good crucible may be briefly outlined under the following heads:

Mechanical.—Crucibles must be sufficiently strong to resist, without bulging, the pressure of the molten material they contain. In many cases, for example, the casting of metals, alloys and glass, they must be rigid at high temperatures, so that they can be lifted and handled by tongs, or some gripping device, without failure. The requisite strength can be secured by using, say, a suitable clay, such as those from Stourbridge, Derbyshire, Klingenberg and certain localities in France and Belgium; by correct grading and proportioning of the grog and admixed materials, by avoidance of cracks and strains during manufacture, by careful firing, and by attention to shape and design. As a rule, attempts to increase mechanical strength by incorporating fibrous material, such as asbestos, in the wall, or by binding the wall with metal hoops, have not been successful.

Physical.—Texture, a property which can be controlled by the grading of the component materials, must be selected according to the purpose for which the crucible is to be used. A close interlocking texture is essential for mechanical strength, for preventing permeation by molten material, and is generally stated to favour heat conductivity. In using crucibles for casting, however, they are often completely removed from the furnace and thus subjected to an abrupt change of temperature which renders them liable to fracture. In the case of clay materials, resistance to this is secured by the use of a relatively large proportion of coarse grog (possibly 30 to 50% of a grade retained on an ⅛-in. sieve). Such an admixture, coupled with exclusion of finer and intermediate grades, increases the porosity and the tendency to penetration, so that in this, as in many other points, a compromise must be struck. Compared with metals, the heat conductivity of refractory materials is low, though in crucibles in most cases the opposite quality would be a great advantage and it is largely for this reason that graphite and carborundum have been used extensively.

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[1] Owing to a confusion in the nomenclature, the seeds and oil discussed in the papers quoted were incorrectly described as from *C. Elliotianus* Baill., which is a related Madagascan species (Priv. comm. from Imperial Institute, 1937).

CHEMICAL.—The main chemical considerations are the relation of chemical composition to refractoriness and to the resistance to the attack of molten metals, slags, etc. The refractoriness depends not only upon the low content of fluxes, such as alkalis, iron compounds, etc., but also on the ratio of the more infusible oxides to one another. For example, the addition of silica to some clays may reduce the refractoriness of the mixture. Occasionally, on the other hand, a small amount of somewhat fusible material is added to favour vitrification and thus diminish the risk of permeation of a crucible. R. H. Stone (J. Amer. Ceram. Soc. 1933, **16**, 96–101) considers that the presence of a certain amount of flux (felspar) in the Klingenberg clay accounts for its suitability for graphite crucibles. Apart from chemical composition, the temperature at which a crucible begins to soften or melt is influenced by other factors, such as grain size, the finer grains appearing to be more fusible, and by the character of the atmosphere in which they are heated, a reducing atmosphere generally tending to lower the refractoriness.

Resistance of the inside of a crucible to chemical attack by molten metals, slags, salts, etc., is obviously a very complex and wide question. The general principle of using an acid (silicious) refractory in contact with an acid material, and a basic (aluminous, magnesian) with a basic, holds good. In many cases, however, crucibles are composed largely of neutral refractories, such as graphite and carborundum, that is to say, those which do not tend to combine with either acid or basic material, a fact which limits the range of attack to some extent. In addition to the selection of a suitable crucible for a particular purpose, on the lines just indicated, increased protection is often provided by lining the crucible with a layer of some specially resistant material. Assuming that the layer adheres satisfactorily, this procedure has the advantages that specific resistance to individual forms of chemical attack is provided and the inherent properties of the crucible, such as a coarse texture, can be retained and consequent permeation of the wall restricted, by developing a dense and compact layer on the inside. The following quotation from Percy ("Metallurgy," 1875, p. 141) is of interest: " Lining or Brasquing Crucibles with other than Carbonaceous Matter." Berthier (Traité des Essais, Paris, 1834, i, 83) states that he has occasionally lined crucibles with silica, alumina, magnesia or chalk, previously moistened with water, so as to make them sufficiently cohesive, and that a thin lining of chalk renders earthen crucibles less permeable to molten litharge." From this it appears that at that time the advantages of a carbonaceous lining were recognised, but that other materials could be used in special cases. The term " earthen crucibles " was applied to what would nowadays be described as " clay crucibles." Also, the mention of molten litharge suggests some points with regard to the destruction of crucibles by molten material. Many metals have little effect, but various salts and slags either permeate the wall or exert a definite solvent action on it. In this connection reference may be made to the section on slags in Percy's " Metallurgy " (pp. 46–86), in which the action on clay crucibles, of slags of varying composition, is specifically described in several cases. From a large number of suggestions, the following are mentioned as illustrations. For crucibles made of refractory clay and sand for metallurgical use, Queneau claimed the use of linings of refractory clay mixed with a substance capable of resisting the chemical operations concerned, and firmly compressing the lining before firing (F.P. 354319, 1905; J.S.C.I. 1905, **24**, 1071). For aluminium alloys, Frary claims a lining of finely ground alumina, bonded with sodium silicate (U.S.P. 1572475; J.S.C.I. 1926, **45**, 330). For the " Thermit " process, Goldschmidt recommended lining crucibles with a mixture of soluble glass with magnesia and corundum (F.P. 354597; J.S.C.I. 1905, **24**, 1114). Deppeler claims to make the thickness of the crucible wall sufficient to remove so much heat of the reaction that a thin layer of slag is formed on the inner surface as soon as reaction begins (U.S.P. 1530395; J.S.C.I. 1925, **44**, 408). Crucibles may be rendered non-porous by treating with ferrous sulphate solution and firing (Mitchell, U.S.P. 894845; J.S.C.I. 1908, **27**, 886). Satô suggests soaking alumina crucibles (for a Tammann furnace) in an aqueous solution of aluminium chloride and heating to above 345°C., the temperature of decomposition of the salt (B. 1935, 804). The fracture of crucibles by expansion of solidifying metal can be prevented by lining with friable material (Colby, U.S.P. 830208; J.S.C.I. 1906, **25**, 934). For preparing fused quartz, Keyes suggests lining a carbon crucible with a paste of sodium tungstate and an appropriate binder; the paste is spread over the inner surface of the crucible which is then ignited in order to harden the lining, and this is treated with a burnishing tool or roller to give it a firm and compact surface (U.S.P. 1249637; J.S.C.I. 1918, **37**, 89A).

CLASSIFICATION, COMPOSITION AND MANUFACTURE OF CRUCIBLES.—The following simple classification, which is adequate for most purposes, arranges crucibles under the heads:

Clay Crucibles.
Carbonaceous Crucibles.
Crucibles of Miscellaneous Materials.

Clay Crucibles are probably the oldest and have been used very largely for the melting of metals, alloys and glass. The chief varieties are known under special names which are still retained, and the following descriptions, taken mainly from Percy's "Metallurgy," may be quoted. The clays generally used in this country are certain varieties from Stourbridge, Stannington and Derby (*v. infra*). A mixture of raw ground clay and about half its weight of graded grog, made from old glass-house pots from which all adherent glass has been removed, is used. The smaller crucibles are fired in a kiln, but the large casting pots are baked immediately before use, and very hard-baked crucibles are more liable to fracture on reheating. A very plastic clay, such as Dorset ball clay, which enables a large amount of grog to be incorporated, is sometimes substituted for a part or even the whole of the pot clay.

Cornish Crucibles, largely used for copper assaying are, according to Searle, composed of 1 part of Teignmouth ball clay, 1 part of Poole ball clay, and 2 parts of St. Agnes' Beacon Sand. They can be heated suddenly, but are not refractory enough for melting steel. Crucibles of this name are now made by the Morgan Crucible Company of Battersea.

London Crucibles are round in shape, fine grained, withstand the action of litharge fairly well, but do not stand sudden changes of temperature. The name refers actually to the shape rather than the composition or place of manufacture.

White Fluxing Pots, also made by the Morgan Crucible Company, from a highly refractory fireclay from Rouen, have a very smooth surface, resist the action of fluxes well, but crack with sudden changes of temperature.

Hessian Crucibles, largely used for melting precious metals and chemicals, are triangular in cross-section and are of varying sizes which fit into one another to form a "nest." They are somewhat porous, rapidly attacked by litharge, and very liable to fracture with abrupt changes of temperature. According to Searle, they are made of 2 parts of Gross Almerode clay and 4 or 5 parts of Epterode sand; the clay melts at Seger cone 33 to 34 and has the approximate composition:

	%
Silica	64
Alumina	24
Loss on ignition . . .	7
Iron oxide, lime, etc. . .	5

They are obviously acid in character and in many ways resemble Cornish crucibles.

French Crucibles are made from 1 part of clay (Ardennes) and 2 parts of the same clay fired as grog or chamotte. They are refractory, fine grained, and resistant to slags.

Silica Crucibles may be made by mixing sand or powdered silica with an absorbent material, *e.g.* kieselguhr (Sankey, B.P. 3353, 1906; J.S.C.I. 1907, **26**, 96), or with cement and water and, after drying, heating to the fusing point of silica (Reppey, U.S.P. 905295; J.S.C.I. 1909, **28**, 24), or with a little lime (Berglund, F.P. 366830; J.S.C.I. 1906, **25**, 1081).

The tables shown on p. 438 give the composition of some clays used for crucibles and of various types of crucibles.

Carbonaceous Crucibles.—It has long been recognised that the incorporation of carbon with the clay of crucibles diminishes their tendency to break with sudden changes of temperature and increases the heat conductivity without lowering the refractoriness. Carbon is generally introduced in the form of graphite, which should have a low content of mineral matter and a suitable texture. The ash should not exceed 5 to 10% and must be infusible and have no tendency to combine with the clay to form a fusible mixture. In texture, graphites consist mainly of thin flakes or of irregularly shaped grains; the former tend to give a mixture which is "slippery," whereas the latter tend to pack closely, especially if grains vary in size. Graphite which has been imported during the past hundred years from Ceylon is particularly suitable. It contains about 95% of carbon and the grains are irregular in shape and size, ranging from minute particles up to several millimetres along their maximum dimension. During the last thirty years graphite has been imported from Madagascar and yields about 80 to 90% of carbon; the flakes are somewhat straight-edged and approach parallelograms or polygons in form (Thiessen, J. Amer. Ceram. Soc. 1919, **2**, 508; Muller, Ber. deut. Keram. Ges. 1935, **16**, 410).

For the manufacture of crucibles, the graphite is ground, sifted, digested with dilute sulphuric acid to remove the greater part of the iron, and mixed with water and kneaded to a stiff paste with about an equal weight of finely ground clay. The mixture is passed through a pug-mill and cut into blocks. When required for use, the blocks are again passed through the mill, and then shaped, dried, and fired in saggers. The shaping may be done by hand, or by "throwing" on a potter's wheel, or by pressing in a mould by hand or mechanical power. Various moulds have been designed for the purpose, and the selection of any one is determined by the size or other properties required in the crucible. A common form consists of a large block of wood (or iron) with a deep cavity, the curved surface of which gives the shape to the outside of the crucible. The block is known as a "flask," and is partly filled with the clay mixture into which a plug or "stopper" is forced with a rotary movement, and thus shapes the inside of the crucible, the space between the flask and the stopper being filled with clay which forms the wall of the crucible. At the bottom of the stopper is a pin, or pivot, which fits into a hole in the bottom of the flask, and the hole thus left in the base of the crucible has to be filled up very carefully when the moulded piece is withdrawn. Crucibles, like other ceramic articles, are also made in jiggers and jolleys, which shape a mass of clay into the required form on the outside and inside. Lastly, crucibles are made by the casting process, in which a slip is poured into a plaster of Paris mould. The surfaces of the best quality crucibles are finished by rubbing with a wet sponge or leather which produces a smooth and less pervious layer on the surface.

Crucibles in which carbon is the predominating constituent have been made in various ways. Small crucibles have been made by turning out of a solid block of gas-carbon on a lathe, and by moulding mixtures of anthracite, charcoal, Analyses of some Clays used for Crucible Making.

	I.	II.	III.	IV.	V.	VI.
SiO_2 . . .	79·25	48·04	45·73	48·08	65·98	49·12
Al_2O_3 . . .	13·57	34·47	34·14	36·89	23·37	35·73
MgO . . .	0·42	0·45	0·74	tr.	0·53	0·24
CaO . . .	0·08	0·66	0·79	0·55	0·41	0·18
K_2O . . .	—	1·94	0·45	1·88	0·76	1·46
Fe_2O_3 . . .	1·38	3·05	(FeO) 1·76	2·36	2·32	0·56
			(FeS_2) 0·77			
Na_2O . . .	—	—	—	—	—	0·39
TiO_2 . . .	—	—	—	—	—	0·11
Loss on ignition	5·11	11·15	10·17	10·87	6·84	11·95
					(S) 0·05	
			Moist. 4·45			
			Org. 0·70			
	99·81	99·76	99·70	100·63	100·26	99·74

I. Stourbridge (Percy).
II. Stannington, near Sheffield (Bischof, "Gesammelte Analysen").
III. Edgemont, near Sheffield (Percy).
IV. Edensor, near Derby (Percy).
V. Gross Almerode (Bischof, "Gesammelte Analysen").
VI. Ball Clay (Mellor and Heath, Trans. Ceram. Soc. 1909, **7**, 151).

Composition of Certain Varieties of Clay Crucibles.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO_2	64·6	72·3	70·9	71·0	65·2	67·4	68·0	72·39	53·92
Al_2O_3	34·4	19·5	24·8	23·0	25·0	32·0	29·0	25·32	40·57
Fe_2O_3	1·0	3·9	3·8	4·0	7·2	0·8	2·2	1·07	—
MgO	—	—	tr.	—	tr.	tr.	0·5	tr.	—
		H_2O 1·8						CaO 0·38	
								K_2O 1·14	S 0·23
	100·0	97·5	99·5	98·0	97·4	100·2	99·7	100·30	94·72

I. French, made by Beaufay at Paris (Berthier, quoted by Percy).
II. French, made by Deyeux at Savignies (Berthier, quoted by Percy).
III. Hessian (Berthier, quoted by Percy).
IV. English steel (Berthier, quoted by Percy).
V. St. Etienne steel (Berthier, quoted by Percy).
VI. Glass pots, Nemours (Berthier, quoted by Percy).
VII. Glass pots, Bohemia (Berthier, quoted by Percy).
VIII. Cornish, made by Juleff (Dick, quoted by Percy).
IX. Steel crucible, clay (Brand, quoted by Percy).

gas-carbon, etc., often with an addition of tar (Putz, D.R.P. 181979; J.S.C.I. 1907, **26**, 1030). Digby recommends the following composition:

Plumbago, 17-mesh granules	17 parts.
Plumbago, 80-mesh granules	2 ,,
Russian clay	5 ,,
China-stone	5 ,,
Gas carbon	2 ,,

The last three ingredients are ground and mixed with water and then the plumbago is added and the crucibles formed, dried at 65°, and baked (B.P. 3661, 1893).

W. Smith (B.P. 149440, 1919; J.S.C.I. 1920, **39**, 658A) saturates porous clay crucibles with a suitable hydrocarbon, and decomposes this by heat in the absence of air, whereby the carbon is deposited in the pores. "Salamander" crucibles, made by the Morgan Company, contain a smaller amount of carbon and resist sudden temperature changes well.

The table on the next page gives the composition of some carbonaceous crucibles.

Carbonaceous crucibles, besides being highly refractory and resistant to sudden changes of temperature, ensure that material in them is melted under reducing conditions, and in the case of steel, for example, may be the means of introducing more carbon (Brand, Chem. Zentr. **15**, 407; Dingl. poly. J. 1885, **256**, 229). Although the carbon is, of course, burnt away during heating in a furnace, the more fusible

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	18·60	40·43	20·0	34·50	25·5	39·77
SiO_2 . . .	42·78	24·63	51·4	45·10	50·0	38·73
Al_2O_3 . .	34·71	27·89	22·0	16·65	20·0	16·54
Fe_2O_3 . .	—	—	3·5	0·95	1·5	1·70
CaO . . .	—	—	0·2	—	0·5	0·85
H_2O . . .	—	—	1·8	2·50	3·0	0·70
Sulphur . .	0·49	0·27	—	—	—	—
						TiO_2 0·52
						MgO 0·34
						K_2O 1·02
	96·58	93·22	98·9	99·70	100·5	100·17

I. Steel crucible, coke clay (Brand, quoted by Percy).
II. Steel crucible, graphite (Brand, quoted by Percy).
III, IV, and V. English blacklead (Mene, quoted by Percy).
VI. Salamander (Hancock).

mineral constituents in some cases form a protective glaze over the carbon particles. This object may also be achieved by coating the crucible with clay and borax, etc. (Woolford, B.P. 24479, 1898; J.S.C.I. 1900, **19**, 52; McDonald, U.S.P. 828954; J.S.C.I. 1906, **25**, 119).

Crucibles of Other Refractory Materials.—So many different refractory substances have been suggested for the manufacture of crucibles that only a few illustrative examples can be given. On account of its refractoriness, alumina has often been used. Deville (Ann. Chim. Phys. 1856, [iii], **46**, 195) employed a mixture of strongly calcined and gelatinous alumina, and also in place of the former, a material made by calcining an intimate mixture of alumina and powdered marble. Generally, crucibles are made from strongly calcined alumina, or bauxite (*q.v.*), mixed with a refractory clay as binding agent. Caspar (U.S.P. 886111; J.S.C.I. 1908, **27**, 568) shaped small pieces of amorphous aluminium hydroxide by the addition of water and then drying and firing them to a white heat, in a closed vessel. In some cases he added pure magnesia and thus typified many attempts on the same lines to form a spinel to act as a binding agent. Fused alumina, in the form of alundum (*q.v.*) or corindite (*q.v.*) has been used for crucibles, generally with a refractory clay as binder.

The fibrous character of asbestos suggests that its use would be advantageous in strengthening the walls of vessels containing molten matter and subjected to handling. Havard ("Refractories and Furnaces," p. 228) recommends mixtures of fireclay, graphite, etc., with asbestos for crucibles. At the same time it must be borne in mind that under the action of prolonged heating, asbestos tends to disintegrate and lose its binding power.

Carborundum crucibles are very refractory, mechanically strong, and resistant to chemical attack. Generally they are made from a mixture of carborundum with a highly refractory clay to give a plastic mass (Velter, F.P. 376179; J.S.C.I. 1907, **26**, 1010; Engels, B.P. 14567, 1901; J.S.C.I. 1902, **21**, 1081). Many other substances have been used, such as glue, water-glass, etc.; thus, a mixture of carborundum and ganister is pressed into shape and then heated in an electric furnace (Imray and Carborundum Co., B.P. 19493, 1902, and 3308, 1903; J.S.C.I. 1903, **22**, 213, 698). A strong and very resistant material has been made with 68 parts of silicon carbide, 25 parts of flake or crystalline graphite, 7 parts of clay, and a carbonaceous binder, such as tar, pitch or molasses, or part of the clay may be replaced by a flux such as borax (Buffalo Refractory Corp., B.P. 176436, 1920; J.S.C.I. 1922, **41**, 328A).

Purified and powdered chrome iron ore, mixed with fireclay to which aluminium hydroxide has been added, may be moulded into crucibles and burned, with or without the addition, before burning, of a substance rich in carbon, such as sugar, resin or coal (Bach, B.P. 24041, 1903; J.S.C.I. 1904, **24**, 64; Klein, U.S.P. 787770; J.S.C.I. 1905, **24**, 547). By applying a chromium salt to the inside of a crucible and then firing, a lining of sesquioxide of chromium is produced (Placet, B.P. 28728, 1896; J.S.C.I. 1897, **16**, 919).

Lime crucibles have been made from lumps of well burnt, preferably slightly hydraulic, lime by turning on a lathe. The lime may be soaked in molten paraffin wax, resin or tar to prevent slaking (Searle, "Refractory Materials," p. 471). Larger crucibles may be made by compressing a layer of lime round the inside of a clay crucible, which has been coated inside with graphite in order to prevent combination of the silica and lime at high temperatures (Percy, "Metallurgy," p. 134).

According to Percy (*op. cit.* p. 135), magnesia was introduced by Caron as a basic material for making crucibles and for lining reverberatory furnaces for melting and dephosphorising steel (Compt. rend. 1866, **62**, 296). The magnesite was obtained from the island of Euboea and must be very strongly calcined to prevent subsequent shrinkage in use, and is mixed with 15–30% of lightly calcined (decarbonated) material and water to form a paste which is moulded, strongly compressed, dried, and fired at a red heat. It is interesting to note that

Gaudin is stated to have made crucibles from a mixture of 1 part of magnesia and 1 part of bauxite, which would presumably yield an artificial spinel, and is indicative of several recent investigations on basic refractories (*e.g.* Chesters and Parmalee, J. Amer. Ceram. Soc. 1935, **18**, 94; J.S.C.I. 1935, **54**, 454B). Crucibles may also be made from a mixture of calcined magnesite with from 2 to 12% of a boron compound, moistened, moulded, dried, and fired at a high temperature (Rawson and Littlefield, B.P. 16004, 1900; J.S.C.I. 1901, **20**, 992; *ibid.* 1902, 52). The product is said to resist molten litharge. Crucibles of a similar mixture may be rendered porous by the addition of sawdust (Dobell, B.P. 10715, 1897; J.S.C.I. 1898, **17**, 461). According to Havard (*op. cit.* p. 237) crucibles of magnesia—and other refractory oxides—are made by electrically fusing the material (Weintraub, Met. and Chem. Eng. 1912, **10**, 308). A layer of strongly calcined magnesia, finely ground in a tube-mill, is spread on the bottom of a carbon or graphite mould. A carbon plug, covered with a thick layer of paper to allow for the subsequent shrinkage of the magnesia, is inserted, and the space between it and the wall of the mould filled with powdered magnesia and the whole heated in an electric furnace to 1,500°C. (U.S.P. 1022011, 1912). A similar method is given by Kerl ("Handbuch der gesammten Thonwaaren Industrie," p. 963); powdered magnesia is filled into a carbon tube, fitted between two carbon blocks, the lower of which is cut to shape the inside of the article, and on passing the current the magnesia fuses and runs down over the shape.

Small crucibles, usually for laboratory work, have been made from such refractory oxides as zirconia, thoria, ceria, etc. (*see further*, Percy, "Metallurgy" (Fuel, etc.), 1875, pp. 110–141; B. Kerl, "Handbuch der gesammten Thonwaaren Industrie," 1907, pp. 932–965; Searle, "Refractory Materials," 1924, pp. 464–503; Havard, "Refractories and Furnaces," 1912, pp. 228–238; C. Bischof, "Die feuerfesten Tone," 1923, pp. 178–193).

W. C. H.

CRYOGENINE. Phenylsemicarbazide antipyrine.

CRYOLITE. (Ger. *Kryolith.*) A native fluoride of aluminium and sodium, found almost exclusively in Greenland, whence it has been sometimes called "Greenland spar." The name cryolite, or "ice-spar" (*Eisstein*), refers to the general resemblance of the mineral to ice (*κρύος*) and to its ready fusibility in a candle-flame. The mineral was discovered by the Danes in 1794, and described by Schumacher in 1798. All the cryolite used in commerce is obtained from a single locality at Ivigtut (or Evigtok), on Arsuk-fjord in south-west Greenland. This locality was visited by Giesecke, and later by J. W. Tayler (Quart. J. Geol. Soc. 1856, **12**, 140). The cryolite occurs as a large deposit in gneiss, and contains (especially near its junction with the enclosing rock) a number of metallic minerals, such as galena, pyrites and chalybite (*v.* P. Johnstrup, N. Jahrb. f. Min. 1886, i, Ref. 28; R. Baldauf, Z. pr. Geol. 1910, **18**, 432: O. B. Bøggild, Mineralogia Groelandica, Kjøbenhavn, 1905; O. B. Bøggild, Meddelelser om Grønland, 1912, **50**, 107, and Z. Kryst. Min. 1913, **51**, 591; C. P. Bernard, The Cryolite Mine at Ivigtut, Greenland, Mining Magazine, 1916, **14**, 202).

Cryolite is usually found as cleavable translucent masses, of snow-white colour, with a peculiar moist-looking vitreous lustre which renders the mineral easy of recognition. H. 2½, sp.gr. 2·9–3·0. Crystals are rare; they are cube-like in habit, and belong to the monoclinic system, with three perfect cleavages approximately at right angles to one another. Although cryolite is usually white, it is sometimes coloured brown or reddish, and is said to pass downwards, in the Greenland deposit, into a black mass. The black variety loses its colour when heated. Before the blowpipe cryolite fuses to a white enamel.

The composition of cryolite may be represented by the formula $3NaF{\cdot}AlF_3$ or Na_3AlF_6. This corresponds to Al 12·8, Na 32·8, F 54·4%. An analysis of the Greenland cryolite by Chodney yielded Al 13·23, Na 32·71, Mn_2O_3 and MgO 0·83% (Verh. Russ. Min. Ges. 1846, for 1845–46, 209). Durnev found in the cryolite of Miask in the Urals, Al 13·41, Na 32·31, Fe_2O_3 and Mn_2O_3 0·55, CaO 0·35% (Pogg. Ann. 1851, **83**, 587). Deville found in the Greenland cryolite 0·018% of vanadic acid and a small proportion of phosphoric acid. An analysis of cryolite from near Pike's Peak, Colorado, by Cross and Hillebrand yielded Al 12·9, Na 32·4, F 53·55, Fe_2O_3 0·4, Ca 0·28, H_2O 0·3% (Amer. J. Sci. 1883, **26**, 271).

Cryolite was formerly a rare mineral, but about 1855 it was introduced into Europe commercially, and at once found numerous applications in the arts. About 10,000 tons are exported annually from Greenland. By heating finely powdered cryolite with sodium or with magnesium, J. Percy and A. Dick obtained metallic aluminium (Phil. Mag. 1855, **10**, 364). Deville found that fused cryolite is decomposed by the passage of an electric current, with elimination of free aluminium. At the present time, aluminium is prepared by the electrolysis of bauxite, but the addition of some cryolite is necessary to start the process and to keep it in continuous operation (*v.* ALUMINIUM).

A wide range of applications was suggested when Julius Thomsen showed in 1850 that cryolite is readily decomposed by heating with calcium carbonate, and that sodium aluminate may be thus obtained:

$$Al_2F_6{\cdot}6NaF+6CaCO_3 \\ =3Na_2O{\cdot}Al_2O_3+6CaF_2+6CO_2$$

If heated with quicklime, a similar decomposition is effected. The sodium aluminate has been used in the manufacture of alum, and in the preparation of caustic soda for soap making. By lixiviation, the aluminate is easily dissolved out; and by the passage of CO_2 through the solution, Na_2CO_3 is obtained, while alumina separates in a gelatinous form. The decomposition of cryolite may also be effected by boiling the finely pulverised mineral with milk of lime. By adding an excess of powdered cryolite to the resulting solution, the aluminate is decomposed, the alumina being precipitated, while sodium fluoride remains in solution:

$$3Na_2O{\cdot}Al_2O_3+Al_2F_6{\cdot}6NaF \\ =2Al_2O_3+12NaF$$

Cryolite can be readily decomposed by the action of sulphuric acid, with formation of sodium sulphate, which can be easily converted into carbonate ; but the process, after trial at Copenhagen, has been abandoned in consequence of the inconvenience arising from the evolution of hydrofluoric acid :

$$Al_2F_6{\cdot}6NaF+6H_2SO_4 \\ =Al_2(SO_4)_3+3Na_2SO_4+12HF$$

The manufacture of soda from cryolite is carried on at Oersund in Denmark, and at Natrona, near Pittsburg in Pennsylvania. The mineral is also employed in the preparation of enamels on iron and for the manufacture of an opaline glass, somewhat resembling porcelain. This glass may be formed by fusing together 100 parts of silica, 35 or 36 of cryolite, and 13 or 14 of oxide of zinc. C. Weinreb has investigated the cause of the milkiness of cryolite glass, and believes that it is due to the presence of aluminium fluoride, which, on cooling the fused mass, separates in a highly comminuted condition, and being distributed through the glass renders it more or less opaque (Ding. Poly. J. 1885, **256**, 361).

L. J. S.

CRYOLITHIONITE. Fluoride of lithium, sodium and aluminium, $Li_3Na_3Al_2F_{12}$, remarkable in containing a higher percentage of lithium (5·35%) than any other mineral. It occurs as large, colourless, rhombic-dodecahedra embedded in the cryolite deposit at Ivigtut in Greenland. Sp.gr. 2·77, H. 2½–3, n_{Na} 1·3395, m.p. 710°. The mineral dissolves in 1350 parts of water at 18°, and from this solution crystallises as cubes.

L. J. S.

CRYOSCOPY. As early as 1788 Blagden proved that the extent to which the freezing-point of an aqueous solution lies below that of water—the depression of the freezing-point, as it is called—is proportional to the concentration of the dissolved substance. Nearly a century later, the researches of de Coppet and Raoult showed that when equimolecular proportions of different substances are dissolved in equal quantities of a given solvent, the solutions so obtained have, in general, the same freezing-point. It is on these facts that the use of the cryoscopic method of determining the molecular weights of dissolved substances is based.

In comparing the effects of different substances on the freezing-point of a given solvent it is obviously convenient, in view of de Coppet's and Raoult's results, to refer these effects to 1 g.-mol. of solute and to some definite quantity of the solvent; in practice, 100 g. of the latter is taken as the standard amount. The depression of the freezing-point for such a concentrated solution as one containing 1 g.-mol. of solute in 100 g. of solvent cannot be determined directly; it is calculated from the depression observed for a dilute solution, on the basis of the proportionality between depression and concentration. The depression, therefore, for a solution containing 1 g.-mol. of non-electrolyte in 100 g. of water is a constant, independent of the particular solute; the average value of the cryoscopic constant for water is 18·5°.

For each solvent, a characteristic figure can be similarly deduced from experimental data. The evaluation of this constant—the molecular depression of the freezing point—is effected by substituting experimental values in the formula. $K=\frac{M}{g}\cdot\Delta t$, where Δt is the depression of freezing-point observed for a solution containing g grams of solute in 100 g. of solvent, and M is the molecular weight of the solute.

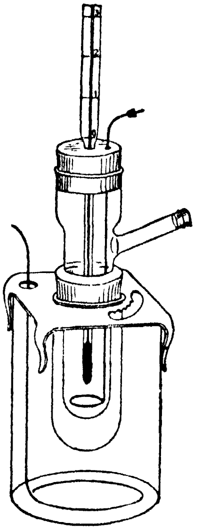
It has been shown by van't Hoff that, on thermodynamical grounds, the molecular depression of the freezing-point for any solvent is quantitatively related to the temperature of freezing and to the latent heat of fusion. The relationship in question is $K=\frac{0{\cdot}0198T^2}{w}$, where T is the freezing-point of the solvent on the absolute scale, and w is the latent heat of fusion per g. of the solvent. The following table shows how far the values of the molecular depression calculated for various solvents by van't Hoff's formula, are in agreement with those deduced empirically :

Solvent.	K (found).	K (calculated).
Water	18·5	18·6
Acetic acid	39	38·2
Phenol	53	50·5
Benzene.	51·2	50·7
Naphthalene . . .	69	69·5
Camphor	400	—
Camphorquinone . .	457	—

The van't Hoff formula assumes that the solution is an "ideal" one and that pure solvent only crystallises from it. Should the latter condition not obtain the whole method breaks down, the depressions observed being always too low. An examination of the van't Hoff formula was made for a number of solutions by Hückel, Kumetat and Severin (Annalen, 1935, **518**, 184) and the abnormalities were shown to be due to the formation of mixed crystals of solvent and solute. Attempts have been made to connect the constant with other properties of the solvent and have been successful in certain cases. Thus J. F. Durand and L. Waï-Hsun (Bull. Soc. Chem. 1936, [v], **3**, 1389) showed that the following relation applied to a number of organic substances, K=·0015 MT, where K was the cryoscopic constant, T the absolute melting-point, and M the molecular weight.

Two main uses of the cryoscopic method must be clearly differentiated. The first as a means of finding approximate molecular weights, which has its main application in organic chemistry, and the second as a method of investigation in the study of the properties of solutions. For the latter work the highest accuracy is necessary and consequently complicated apparatus is employed, whereas for the former purpose an accuracy of a few per cent. is sufficient and ease and speed of working are important factors. The Beckmann and Rast methods, which are capable of an accuracy of about 2–5%, will be first described and afterwards an outline given of modern precision methods.

The Method of Beckmann.—Essentially the procedure is to compare the freezing-point of the pure solvent and solution using a thermometer that is calibrated to read differences and not absolute temperatures. Such differences can be measured with much greater accuracy than the actual freezing-points, and this fact is utilised in all cryoscopic determinations. The thermometer has a very open scale which covers only 5–6°C. in a length of about 20 cm.; consequently it can be divided into divisions of 1/100°. These divisions can be subdivided by eye to 1/1,000° with the aid of a special lens which slides on the stem of the thermometer and enables errors from parallax to be avoided.



A reservoir is attached to the upper end of the thermometer tube so that the quantity of mercury in the bulb may be varied. This permits the thermometer to be used for different temperature ranges and hence with various solvents. The adjustment of the amount of mercury in the bulb is carried out as follows. The thermometer is inverted so that the bulb is pointing vertically upwards and gently tapped so that the mercury in the bulb begins to flow down the thread and into the reservoir, where it is united with any metal that already happens to be there. The thermometer is then turned very carefully and the bulb placed in a bath 2–3°C. above the highest temperature at which it is proposed to work. Provided this operation is done without vibration the mercury will remain joined through the thread from the reservoir to the bulb and sufficient mercury will flow into the bulb to fill it at the bath temperature. The thermometer is then given a sharp tap with the finger which detaches the excess mercury in the reservoir and the thread will be found to be at the top of the scale at the required temperature. If during the above operation the mercury thread shows a tendency to break, this may be prevented, by holding the thermometer at an angle of 30° to the horizontal, instead of vertically, while the mercury is flowing from the reservoir into the bulb.

The other essential parts of Beckmann's apparatus are seen in the diagram shown above. A stout glass jar, holding about 1½ litres, is provided with a metal top at the side of which is a hole for a stirrer, and in the middle of which is another hole capable of holding a large, stout test-tube, 3–4 cm. in diameter. The lid and the tube are held firmly in position by the springs. By means of a cork, there is fitted in the tube another, narrower tube, to hold the liquid under investigation. This tube should preferably have a flat bottom, while the part of it which projects beyond the outer jacket is provided with an auxiliary side tube, and is itself widened out at the upper extremity. The cork with which this inner tube—the freezing tube, as it may be called—is fitted carries the thermometer, and allows also free passage to a stirrer. The latter is best made of thin glass rod or of nickel wire. The thermometer must be fitted in an accurately central position, so that the stirrer may be moved up and down without touching the bulb.

At the start of an experiment the freezing tube is charged with a weighed quantity of the solvent, usually 10–20 g., and the jar is filled with water or a mixture of ice and salt, or other suitable liquid, at a temperature 4–5° below the freezing-point of the solvent under examination. The freezing tube, with thermometer and stirrer, is immersed directly in the jar, until the temperature has fallen almost to the freezing point. It is then set in the jacket tube and the contents are stirred regularly, while the mercury in the thermometer falls slowly. The fall continues until the solvent is more or less supercooled. In the majority of cases freezing sets in spontaneously before the supercooling exceeds 0·5°, and the liberation of heat results in a rise of the mercury in the thermometer up to a steady maximum position. This is the freezing-point of the solvent—the temperature at which liquid and solid solvent are in equilibrium with each other. It is advisable, when the thread is rising towards its steady position, to tap the thermometer before taking a reading and so avoid the possibility of the mercury sticking in the capillary. Should the supercooling exceed 0·5°, crystallisation ought to be initiated. This may sometimes be done by vigorous stirring or, better, by introducing a small crystal of the solid solvent. D. E. Kenyon and G. A. Hulett (J. Amer. Chem. Soc. 1934, **56**, 1649) recommend that a small glass bead wetted with the solvent and then cooled in solid carbon dioxide be used in place of the crystal, which is rather difficult to introduce. A third method is to touch the surface of the liquid with a thin wire which has been previously cooled in liquid air. The freezing-point of the solvent having been determined two or three times in the manner just described, a weighed quantity of the solute, enough to give a depression of not less than 0·2°, is introduced, and the freezing-point of the solution is then ascertained in the same way as that of the solvent. Subsequently additions of solute are made and the resulting depressions determined as before. One addition, it is true, yields sufficient data for the calculation of the molecular weight of the solute, but it is desirable to ascertain also whether the concentration of the solute has any definite and notable influence on the value obtained for its molecular weight. It is advisable, further, to redetermine the freezing-point of the solvent at the end of such a series of experiments, and so obtain a guarantee that the zero of the thermometer has not changed appreciably in the course of the work.

In the past suggestions have been advanced for improving the accuracy of the Beckmann apparatus. Many of them are now redundant owing to the other types of apparatus developed for accurate work. Consequently only those errors will be considered which affect the apparatus when used for its legitimate purpose—the measurement of molecular weights with reasonable accuracy. The bulb of the thermometer may change slightly in volume during a series of experiments if it has previously been at a considerably different temperature. If this is due to an ageing process in the glass it is best to keep the thermometer temperature as steady as possible. When the bulb is thin pressure changes will affect the position of the thread appreciably. Barometric changes have been shown to have an effect of 0·0002°. The general precautions to be adopted for a Beckmann thermometer to be read with an accuracy of 0·0005° are discussed at length by H. C. S. Snethlage (Rec. trav. chim. 1933, **52**, 139).

The temperature of the cooling bath is a matter which has to be carefully considered if the freezing-point depression for a dilute solution is to be correctly determined. Suppose that in an experiment with the ordinary Beckmann apparatus the aqueous solution in the inner tube cools without freezing, it is obvious that the lowest temperature to which the solution can fall must be higher than that of the cooling bath, because of the heat conducted from the air to the solution through the thermometer, stirrer, and tube, and because of the heat generated by the stirring. This lowest temperature which the contents of the freezing tube tend to assume when no freezing takes place is known as the *convergence temperature.* The difference between the convergence temperature and the temperature of the cooling bath varies, of course, with each apparatus ; it decreases as the facility for heat exchange between the solution and the external air is lessened, and as the rate of stirring is diminished. Suppose now that the solution under examination has become supercooled, and that it has reached the convergence temperature. The introduction of a crystal of the solid solvent at this stage initiates the freezing process ; heat is liberated and the temperature of the solution rises. Inasmuch, however, as the solution is no longer at the convergence temperature, there is an influence at work tending to lower the temperature of the solution, so that the latter never reaches its true freezing-point; the maximum position reached by the mercury is only what may be called the apparent freezing-point of the solution. Similarly, when the freezing-point of the solution lies below the convergence temperature, an apparent freezing-point is observed which is somewhat higher than the true freezing-point. In both cases the apparent freezing-point lies between the true freezing-point and the convergence temperature. In view of these considerations, it is necessary in cryoscopic work to keep the bath temperature as near the freezing-point as possible. The error is also automatically corrected if a value of K is determined with a substance of known molecular weight under conditions identical with those used for the unknown material.

In choosing a solvent for a molecular weight determination it must be remembered that electrolytes in water will dissociate and give low values, whereas many hydroxylated and other organic compounds may associate in benzene (Bury and Jenkins, J.C.S. 1934, 688). When there is a possibility of these complications determinations must be made in more than one solvent. Some work has been done on cryoscopy in mixed solvents, but the results as yet are more of theoretical than practical significance (*see* O. Anders, Z. physikal. Chem. 1933, **164**, 145; G. Scatchard and S. S. Prentiss, J. Amer. Chem. Soc. 1934, **56**, 1486).

For the determination of the freezing-point of liquids which are obtainable only in small quantities—physiological fluids, for example—Beckmann's apparatus, in its ordinary form, is too large. Modifications of this apparatus, suitable for the investigation of blood, urine, etc., have been suggested by various authors (Guye and Bogdan, J. Chim. phys. 1903, **1**, 379; Burián and Drucker, Zentr. Physiol. 1910, **23**, 772; D. Thomas, Z. ges. exp. Med. 1933, **87**, 635). In these instruments only 1–2 c.c., or in the last 0·1 c.c., of liquid is required, and it is claimed that the accuracy is of the same order as that attainable with the ordinary Beckmann apparatus.

THE MICRO RAST METHOD.—The determination of molecular weights by the Rast method (Ber. 1922, **55**, [B], 1051, 3727) is likely to entirely replace the use of the freezing-point apparatus of Beckmann in the organic chemistry laboratory. It has the advantage of requiring only a very small amount of the solute and the procedure is simpler and quicker than with the older method.

The remarkably high values for the molecular depression of camphor and some related compounds will be noted in the table on page 441*d*. These substances have excellent solvent action for the majority of organic substances and the fact that there is now a number of them available enables the molecular weight to be checked in two or more solvents, thus guarding against errors due to the separation of mixed crystals of solute and solvent and to association of the solute. Essentially the method consists in observing the melting-points in the ordinary capillary tubes of the pure solvent and of a mixture of known composition. This determination can be carried out in the normal fashion as the depression is large enough for an ordinary thermometer to be used for the temperature measurement. It is best, however, to use a good lens for the examination of the mixture while it is melting. One of two methods of procedure may be adopted, the first when an amount of the order of 0·2 g. of the substance under investigation is available and, second, the true micro-method, which requires only a few milligrams.

In the first method about 0·1 g. of the substance is accurately weighed into a small test tube using an ordinary analytical balance.

About ten times this amount of camphor is then added, the tube reweighed, and then sealed off at the blowpipe. The tube is heated in a bath at a temperature slightly above that of the melting-point of camphor and shaken thoroughly until all the solute has dissolved. The tube is removed from the bath and shaken while it is rapidly cooled. Finally it is cut open and the contents powdered in a small agate mortar. Samples of this powder are placed in ordinary melting-point capillary tubes and the determination carried out in the usual fashion; the temperature being noted at which the last trace of solid disappears. The melting-point of the camphor alone is then determined and from the difference the molecular weight of the solute can be found by substitution in the usual formula. The molecular depression constant varies with the sample of camphor and it is necessary to use a value of K that has been actually determined for the sample used. Benzoic acid or naphthalene are the materials that are commonly used for standardisation.

For the successful operation of the second method some knowledge of micro-chemical manipulations and the use of a micro-balance are required. A capillary tube 40 mm. long and 2–3 mm. in diameter is weighed to 0·000001 g., about 0·2 mg. of the unknown substance is placed in the closed end of the tube which is then reweighed, ten times the amount of camphor is introduced and its weight also found. The capillary is then drawn off at about 15–20 mm. from the closed end, the glass being formed into a long fibre by which the small bulb containing the charge can be held. The camphor and the solute are melted together until the latter has completely dissolved and the melting-point of the mixture is then determined. For details of these operations F. Pregl's "Quantitative Micro-analysis" may be consulted (3rd ed., 1937, J. & A. Churchill, Ltd.).

J. Pirsch has been responsible for many improvements in the Rast method in recent years. He has described a modified procedure to be adopted when the molecular weights of volatile compounds are required (Ber. 1932, **65**, [B], 1227); also a large number of new solvents have been examined. These are recommended to check the results obtained with camphor and to be used when the substance is insoluble in, or decomposes at, the melting-point of camphor. The more important of these materials are:

Camphene, m.p. 49°C., K=310 (Pirsch, Ber. 1932, **65**, [B], 862).

Bornylamine, m.p. 190°C., K=406 (Pirsch, Ber. 1932, **65**, [B], 1227). (Specially useful for alkaloids and basic substances.)

Camphorquinone m.p. 190°C., K=457 (Ber. 1933, **66**, [B], 815).

*cyclo*Pentadecanone, m.p. 65·6°C., K=213 (Giral, Anal. Fís. Quím. 1935, **33**, 438). (Used for azo-dyes, also for sterols and derivatives.)

Descriptions of other materials that have been used will be found in the following papers (Ber. 1933, **66**, [B], 1694; 1934, **67**, [B], 1115; 1925, **58**, [B], 2388; Bul. Chim. 1926, [4], **39**, 82; Rocz. Chem. 1933, **13**, 720).

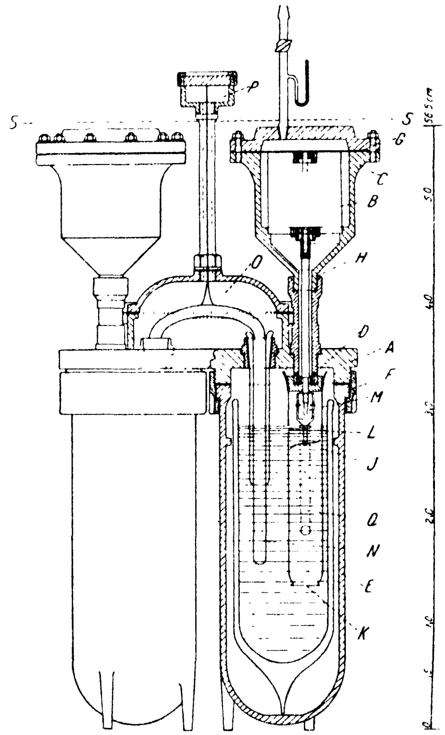
PRECISION CRYOSCOPY.—The modern theories of solution require experimental results of the highest accuracy at considerable dilution for their confirmation. The precise determinations of recent years have all been done in developments of a type of apparatus evolved by Adams (J. Amer. Chem. Soc. 1915, **37**, 481) who used two Dewar vessels, one of which contained 400 g. of ice and 600 g. of water, while the other had similar amounts of ice and solution. The mouths of the vessels were closed with corks and they were supported in a metal can which was nearly filled with ice. The can was closed with a double-walled lid which was also filled with ice. The equilibrium between ice and water or ice and solution required that there be efficient circulation of the liquid. This was accomplished by circulating pumps which were immersed in the Dewar vessels and were operated by glass rods passing through the corks and lid. One-half the liquid was displaced for each stroke of the pump, and consequently equilibrium was rapidly established. The temperature difference between the two Dewar vessels was measured by a 50-junction thermocouple of copper constantan, the wire of which was tested for homogeneity. When the *E.M.F.* was read to one microvolt the temperature could be determined to 0·0001°. After equilibrium had been established some of the solution was withdrawn and its concentration determined with the aid of an interferometer, solutions of nearly equal and known concentration being used for comparison. In this way determinations were carried out with solutions as dilute as 0·004 normal.

F. Hovorka and W. H. Rodebush (J. Amer. Chem. Soc. 1925, **47**, 1614) introduced the following refinements into their apparatus. The mechanical stirrer was replaced by a stream of purified air which was found to give efficient mixing and not cause so much heating as the previous methods. Also, instead of withdrawing and analysing a sample of the liquid, the solution was made up to a known concentration and cooled with the rest of the apparatus to a temperature very close to that of the equilibrium one. The solution was then added to the ice in the Dewar vessel from which the water had been withdrawn a few moments earlier In this way the equilibrium temperature was reached without appreciable change in the concentration of the solution. The temperature difference was measured with a 14-junction thermoelement, and improvements were introduced into the circuit for measuring the potential and excluding parasitic *E.M.F.'s*. This rendered it possible to read the temperature with a precision of 0·00002°.

Randall and Scott (J. Amer. Chem. Soc. 1927, **49**, 647; Randall and Vanselow, *ibid.* 1924, **46**, 2418) surrounded the Dewar flasks with substantial metal casing which enabled the whole apparatus to be exhausted to the vapour pressure of the water, thus excluding the error that may be introduced by changes in the solubility of the air with temperature. The concentration of the solution was found from conductivity measurements. L. Ebert and J. Lange (Z. physikal. Chem. 1930, **149**, 389; 1934, **168**, 147) have introduced further improvements, their final apparatus being shown in the figure on p. 445.

A mechanical stirrer *J* is driven through a device *M* for preventing undue conduction of heat by means of the induction motor *B*. Since the armature of the motor is enclosed in the casing there is no need for packed joints with consequent leakage. The thermocouple *O* is enclosed for the greater part of its length in a Dewar vessel which minimises the conduction of heat down the elements. The concentration of the solution is again found by a conductivity method. Using a 30-junction thermo-element the temperature could be determined to 0·00001°.

Scatchard and Prentiss have also made a series of careful measurements for a variety of alkali salt solutions. Their apparatus is not evacuated but filled with nitrogen which they say does not introduce appreciable errors (*see* J. Amer. Chem. Soc. 1932, **54**, 2676, 2690, 2696; 1933, **55**, 4355; 1934, **56**, 1486, 2314, 2320; 1936, **58**, 837).



The lowering of the freezing-point of non-aqueous solutions has also been considerably developed. L. D. Elliott (J. Physical Chem. 1924, **28**, 611) described an apparatus in which liquid ammonia can be used. The design of the apparatus is similar to that of the ordinary Beckmann apparatus except that the cooling bath is contained in a large Dewar vessel and that arrangements are made for cooling the light petroleum it contains with liquid air. At these low temperatures a resistance thermometer is the best instrument for measuring the temperature. Measurements for ammonium nitrate and sulphuric acid in anhydrous acetic acid have been carried out with an accuracy of 0·0001°C. by W. C. Eichelberger (J. Amer. Chem. Soc. 1934, **56**, 799). F. S. Brown and C. R. Bury (J. Physical Chem. 1926, **30**, 694) have studied the depression of the freezing-point of nitrobenzene by organic compounds. For work with *cyclo*hexanol, *see* E. Schreiner, O. E. Frivold and F. Ender (Phil. Mag. 1929, **8**, 669); with indene, *see* W. Klatt (Z. physikal. Chem. 1934, **171**, 454); and with ether-alcohol mixtures, *see* A. Lalande (Compt. rend. 1932, **195**, 1267). F. Garelli and E. Monath (Atti R. Accad. Sci. Torino, 1926, **61**, 4) have suggested that the cryoscopic method might be employed for the determination of the solubility of gases in organic liquids, and they have determined the solubility of nitric oxide and carbon monoxide in benzene, bromoform and nitrobenzene by this method.

R. H. P.

CRYPTAL. An aldehyde, to which the name *cryptal* was given, was stated to occur in the oils from *Eucalyptus hemiphloia, polybractea* and *Bakeri* (Penfold, J.C.S. 1922, **121**, 266; Penfold and Simonsen, *ibid.* 1930, 403). This substance has now been shown by Berry, Macbeth and Swanson (*ibid.* 1937, 986) to be identical with the ketone, *l*-1-4-*iso*propyl-Δ^2-*cyclo*-hexen-1-one isolated from these oils by Cahn, Penfold and Simonsen (*ibid.* 1931, 1366).

J. L. S.

CRYPTOLITE *v.* CERIUM METALS AND EARTHS, *Monazite*.

CRYPTOPINE, an *iso*quinoline alkaloid.

CRYPTOTAENENE. The aliphatic hydrocarbon, *cryptotaenene*, $C_{10}H_{16}$, b.p. 67–68°/15 mm., d_4^{25} 0·8128, n_D^{25} 1·47476, $[\alpha]_D$ +2·66° occurs in the essential oil obtained from *Cryptotaenia japonica* (Hirano, J. Soc. Chem. Ind. Japan, 1926, **29**, 48). It contains three ethylenic linkages and gives on oxidation with ozone, acetone, formic and succinic acids. Its constitution has not been determined.

J. L. S.

CRYPTOXANTHIN *v.* CAROTENOIDS, *Kryptoxanthin* (Vol. II, p. 399*c*).

CRYSTALLISATION. The researches of William L. Bragg ("Crystallisation," Trans. Inst. Chem. Eng., 1927, **5**, 103–109, and other publications) and others into the crystalline structure of matter have shown that in a crystal the molecules of which it is composed are arranged in a definite space lattice structure and are capable only of oscillatory movement, so that crystalline structure possesses great rigidity and large stresses must be applied to produce plastic flow.

The spacing of the molecules in the lattice, although regular, is not the same in all directions and therefore the forces of attraction between the molecules will vary and result in the crystal possessing different properties along various axes.

Each crystalline substance has its own characteristic arrangement of the space lattice structure and if the crystal is allowed to form freely it possesses a definite geometrical form having a fixed number of plane surfaces which are inclined to one another at definite and characteristic angles.

Many substances are known to adopt two or more wholly different structures depending upon the physical conditions which are prevalent during the growth of the crystal and are termed polymorphic.

Sometimes the conditions required to produce a change in structure are well understood and when they are applied a crystal is obtained which is perfectly stable so long as the conditions, such as a definite transition temperature, are maintained. In other cases the conditions governing the formation of different structures are obscure, the rarer structures being unstable and the crystal either dissolving in the solution or breaking into minute aggregates of the commoner type.

With organic substances it is often difficult to decide whether the modifications in the crystals of a substance are due to polymorphism or to isomerism, that is, permanent intra-molecular differences in structure.

To distinguish between polymorphism and isomerism Sidgwick's (J.C.S. 1915, **107**, 672) method of studying the equilibrium relations between the two forms and a common solvent can be applied, when it will be found that with isomerides differences will survive a process of either solution or fusion.

Crystal Growth.—If it is assumed that the forces of attraction between the molecules constituting the crystal act along lines joining the centres of the molecules, then a diagram can be constructed showing the vectorial distribution of the surrounding field. Molecules within the crystal will be subjected to a balanced system of forces due to the attractions of the surrounding molecules, whereas a molecule at the surface of the crystal will be acted upon by an unbalanced force which tends to attract other molecules to itself or produce a strain at the free surface of the crystal. This surface energy depends upon the number, kind and distribution of the molecules on the plane surface and may vary for different surfaces of the crystal. Moreover, molecules at the corners and edges of the crystal are subjected to smaller attractive forces towards the centre of the crystal and so cannot adhere so strongly to the crystal as those at or near the interior of the plane surfaces. J. Willard Gibbs (" Scientific Papers," London, 1906, p. 325) has indicated that these factors supply much information on the mechanism of crystal growth. When a crystal is immersed in its saturated solution and a state of equilibrium between the crystal and solution is attained the number of molecules arriving at the surfaces of the crystal from the solution must equal the number of molecules leaving these surfaces and entering the surrounding liquid.

A molecule vibrating about an equilibrium position along a line at right angles to the plane surface of the crystal will be subject to an attractive force towards the crystal due to the other molecules forming the crystal and an outward force of attraction due to the molecules constituting the surrounding liquid. If the vibration of the molecule is sufficiently large it may reach a point termed the balance point where the attraction due to the crystal is equal to the attraction of the molecules in the surrounding liquid. Beyond this point the latter force becomes the greater and the molecule tends to enter the solution, but if the vibration of the molecule is not sufficient to carry it to the balance point then the attraction towards the centre of the crystal being the greater force, the molecule will tend to return to the surface of the crystal.

The same theory also applies to the molecules of the solute in the surrounding liquid which not being subject to a directional movement may or may not come sufficiently close to the surface of the crystal to be attracted towards it. The greater the number of the molecules of solute present in the solution surrounding the crystal the greater will be the tendency for these to be attracted to the crystal surfaces. Hence the concentration of the solution is another important factor in crystal growth.

Other factors, in addition to the kinetic energy of the molecule, such as inter-molecular collisions which are dependent upon the number of molecules in the surface layer, and the periodicity of the vibration as well as the dissipation of the heat of solution and the change in density of the solution affect the growing or dissolving of a crystal. As the attractive forces on the molecules at the edges and corners of the crystal towards the centre of the crystal are least the amplitude of their vibrations will be greater than those at the interior of the plane surfaces and therefore the tendency will be for those molecules to leave the crystal and enter the solution. Hence, during the growth of a crystal, complete molecular planes must be formed on the surfaces, and since single molecules at the corners edges or on the surface are held less firmly a definite degree of supersaturation of the surrounding solution is necessary to maintain crystal growth. Before, however, crystal growth can occur there must be a solid nucleus upon which the molecules can be deposited.

Nucleation.—The nucleus upon which the molecules are deposited to form the crystal may consist of a small solid particle inserted in the liquid or may arise by formation of such a particle in the solution by an agglomeration of a number of molecules of the same substance of which the crystal will be composed, to give a small solid particle upon which the molecules can be deposited.

The introduction of small crystals of the substance to be crystallised into the solution in which the growth takes place is known as the seeding of the solution and is sometimes adopted in practice, but the commoner procedure is to form the solid nucleus from the molecules in the solution.

Since the attraction towards the centre of the crystal is least for molecules at the corners or edges, if the particle constituting the nucleus consists of only a few molecules the tendency for these to re-enter the solution is greatly increased (G. A. Hulett, Z. physikal. Chem. 1901, **37**, 385), and therefore such nuclei can only form spontaneously in supersaturated solutions.

Henry Miers and his collaborators (Phil. Trans. 1903, **202**, 459–523 ; Proc. Roy. Soc. 190 **79**, A, 322 ; J.C.S. 1906, **89**, 1013 ;

1908, **93**, 825) by their researches on the concentration of solutions during the progress of crystallisation have contributed materially to our knowledge of the conditions under which nuclei will form spontaneously in a solution, and the requirements which must be fulfilled if crystals of uniform size are desired.

From his observations Miers found that in addition to the ordinary solubility curve A, which divides the area between the X and Y axes into two portions such that if, at any given temperature, the molecular concentration of the solution is represented by a point below the curve A the solution will be unsaturated, if on the curve A saturated, and if above the curve A supersaturated, a second curve B, which has been termed the supersolubility curve, could be drawn which divides the supersaturated area of the diagram into two portions.

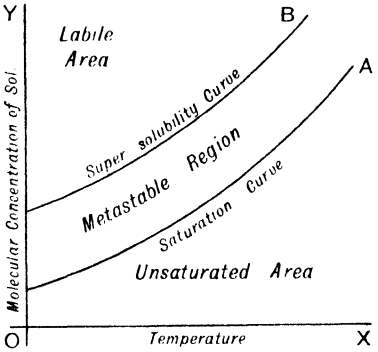


FIG. 1.

The region between the saturation curve A and the supersolubility curve B is one of metastable equilibrium, whilst the region above the supersolubility curve is one of unstable-equilibrium.

If the temperature and molecular concentration of a solution be such that it will be represented by a point in the metastable then it will be found that nucleation will not occur, but if such a solution is " seeded " then these particles will tend to increase in size but not in number.

The metastable region therefore is favourable to the growth of a crystal but not to the formation of the nucleus upon which the growth takes place. On the other hand, if the temperature and molecular concentration of a solution are such as to be represented by a point above the super-solubility curve in the labile region, then it will be found that as long as these conditions are maintained nucleation and crystal growth will occur simultaneously. This will result in a product consisting of a large number of crystals of varying sizes, since the nuclei first formed, being for a longer time in contact with the supersaturated solution, should have grown to a larger size than subsequent nuclei ; the smallest crystals being obtained from the nuclei last formed.

The formation of nuclei by the cooling of a pure solution appears to be a characteristic quality of the molecules, for in some cases only slight undercooling will cause nucleation, whereas with other solutions great undercooling must be employed before the nucleus is formed. As the degree of undercooling increases, nucleation occurs more readily until a maximum is reached, but after this point intense undercooling results in diminished nucleation. Since the mean kinetic energy of the molecules diminishes with fall in temperature if this were the only factor, rate of nucleation would increase with lowering of temperature. Viscosity, on the other hand, regularly increases as the temperature is lowered, and it is therefore assumed that when maximum nucleation takes place the kinetic energy of the molecules and the viscosity of the solution are particularly favourable to the change from isotropic to anisotropic grouping. At lower temperatures the greater vicsosity of the liquid inhibits the change which is also hindered at temperatures above the maximum point by the larger movements of the molecules.

With very rapid cooling it is possible to pass quickly through this point of maximum nucleation and reach a region where the viscosity is so great that crystal formation becomes impossible and when the solution will possess both high viscosity, great rigidity and, at the same time, be isotropic in character.

The rate of nucleation is also greatly modified by the presence of even small quantities of impurities in the solution, some impurities even arresting the formation of the nuclei and others greatly increasing the degree of nucleation (G. Tammann, " The States of Aggregation," New York, 1925, pp. 225–251).

Rapid cooling of the solution usually results in the production of a very large number of very small crystals and industrially this is sometimes of great advantage as in the preservation of food, where in the cold storage of food large crystals would tend to produce rupture of the cell walls.

Crystallisation therefore depends upon two principal factors: (*a*) nucleus formation, and (*b*) subsequent growth of the crystal on the nucleus, and is employed on an industrial scale :

(1) to remove a dissolved substance from solution ;
(2) to separate a dissolved substance from a solution containing other substances;
(3) to produce a dissolved substance from a solution in a marketable form.

(1) *Removal*.—The removal of a dissolved substance from solution can in many cases be effected more economically by evaporation to dryness and where crystallising plant has been installed to remove a dissolved substance its installation was attributable to equipment suitable for complete evaporation not being obtainable.

There are, however, instances in which evaporation to dryness, even with modern equipment, is an uneconomical or impossible means of recovering the dissolved material because of a factor such as the operating temperature being too high, in such cases crystallisation has to be used.

(2) *Separation*.—When the object of the crystallisation process is to separate one

constituent from a solution containing two or more dissolved substances no general rules can be given regarding procedure, for a factor of great importance is the solubility relationships of the various substances present in the solution.

(3) *Production of Marketable Crystals.*—Here the process of crystallisation is employed to produce from a solution, in which it has been dissolved, a solid material for which there is a ready sale.

Within recent years crystals of uniform size have commanded a better market than consignments of the same material in which the sizes of the individual crystals vary greatly. A reason for this demand is that adulteration of a quantity of crystals of uniform size is more easily detected than of a similar consignment consisting of crystals of widely varying sizes, because in the former case the adulterant, if it is not to be easily detected by the eye, must consist of crystals having the same colour, shape and size as the other crystals.

Crystallising Plants.—The production of crystals of a material from a solution in which it is dissolved can be effected in several ways by,

(1) cooling the hot saturated solution ;

(2) evaporating a solution until the concentration of the dissolved substance is such that it will either promote nucleation and maintain subsequent growth of the nuclei or maintain the growth of seeding crystals added to the concentrated solution. This may be carried out at varying pressures either above or below atmospheric. Sometimes evaporation and cooling are combined in order to achieve the desired result; or

(3) other methods, such as by addition of materials which alter the solubility of the dissolved substance in the solution, etc.

Crystallisation by Cooling.

The crystallising pan, one of the earliest forms of crystallisers in which uncontrolled crystallisation by cooling is carried out, is a long rectangular trough made of materials which will resist the action of the solution from which the crystals have to be formed or if attacked by this solution will not spoil the colour of the crystals obtained or mar the product by the presence of too much impurity. Such tanks are often made of cast iron or of wood lined with lead, tin, zinc or other suitable metal, and provided with rounded corners, and having the bottom of the tank sloping towards the outlet. Into such a vessel is run the mother liquor at such a temperature and concentration, which have been previously determined for the particular solution, as will yield the best results. When cooling is complete the liquid is run off and the crystals which are usually adhering to the sides and bottom of the tank removed by hand or mechanical scrapers. Sometimes threads or wires are suspended from rods placed across the tanks upon which crystals are formed, although when threads are used their entanglement, produced by convection currents in the cooling liquid, often results in large crystals of very irregular shapes. Often, too, with this method of crystallisation, irregular crystals are produced by the convection currents carrying very small crystals to the surface of the liquid where they are supported by the surface tension of the liquid until they have grown so large that their weight is greater than this supporting force. During the time that they are thus suspended those surfaces of the crystal which are completely submerged in the liquid will grow in a normal manner, whilst the growth on the other surfaces which are not completely in contact with the liquor will be abnormal. The shape, therefore, of such a crystal will not be regular.

Since in the crystallising pan described above the cooling is effected by (*a*) evaporation at the free surface of the liquid or (*b*) by conduction through the walls of the vessel, and the temperature gradient across the walls is chiefly maintained by the natural convection currents set up within the liquid as it cools, the cooling in this manner is very slow. To increase the loss of heat from the sides of the vessel and so increase the rate of cooling mechanical agitation is often employed. Such a plant for uncontrolled crystallisation by cooling shown in Fig. 2, consists of a cylindrical vessel with an inverted conical base at the lowest point of which is fixed the outlet valve and pipe.

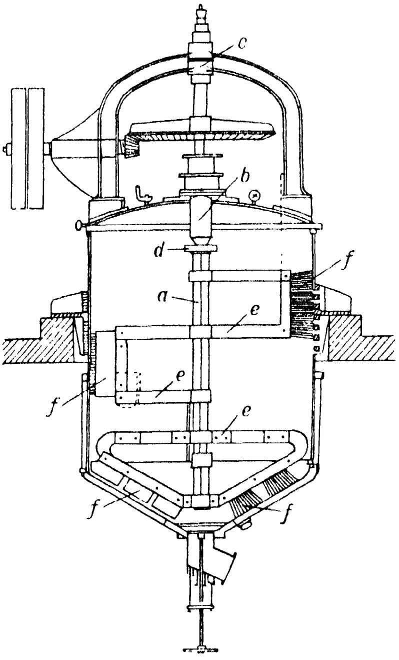


Fig. 2.

Within the cylinder is an agitator *e* carried by a shaft *a* driven by bevel gearing mounted on the cover of the crystalliser which is also provided with an inlet for the mother liquor, a pressure gauge and atmospheric valve, whilst if the solvent is a valuable or harmful material an opening can be arranged for the removal and recovery of the vapour. Since the crystals usually form on the inner surface of the cylindrical shell and reduce the flow of heat from the vessel, Fig. 2 also illustrates a method, namely, by attaching brushes or scrapers *f* to the agitator, of preventing this increased resistance to the flow of heat through the cylindrical walls. The lower portion of this crystalliser is also provided with a jacket through which a cooling liquid can be circulated, and if a highly concentrated solution has to be cooled a strong agitator must be fitted, and in some instances means provided for the removal of the crystals shortly after they are formed.

Another crystallising apparatus, the Passburg, suitable for producing low temperatures such as are used in the formation of crystals of potassium chlorate, is shown in Fig. 3. In this plant the mother liquor enters the left hand crystallising vessel through the pipe K. This vessel is provided with a jacket through which the cooling liquid circulates and to maintain a high coefficient of heat transmission is fitted internally with a set of revolving brushes, J, which remove the crystals from the cooled walls. They then fall into the conical base of this cooler. from which they can be discharged through the valve L into the centrifugal. The cooled mother liquor leaves near the bottom of the vessel, and passing upwards through the inclined pipe M is discharged into the right-hand cooler D. Into this cylinder is fitted a spiral coil C, the lower end of which is coupled to the cooler B, which is connected with the pressure side of the compressor A. The outlet of this coil is at the top and is connected by the pipe E with the suction valves of the compressor; the coil, cooler, and compressor thus constituting a refrigerating system. Brushes arranged on a central shaft which is rotated through suitable gearing P fixed to the cover of this vessel remove the crystals from the surface of the cooling coil. A conical cover is fitted at the bottom of this cooler which collects the crystals removed from the cooling surface. By opening the valve G at the lowest point of this cover, these crystals, together with some of the mother liquor, can enter the centrifugal where separation is effected. The cold liquid leaves this cooler at the bottom and passes to the bottom of a smaller cylinder, H, also fitted with a conical base, having a valve at the lowest point. Whilst slowly ascending this cylinder some crystal growth occurs and this crop of crystals together with some mother liquor is, at regular intervals, discharged into the centrifugal. On reaching the top of this cylinder the mother liquor passes through a pipe into the foot of the jacket of the first cooler. After ascending this jacket and thereby cooling the incoming liquid this cooling solution leaves the crystalliser by the pipe N.

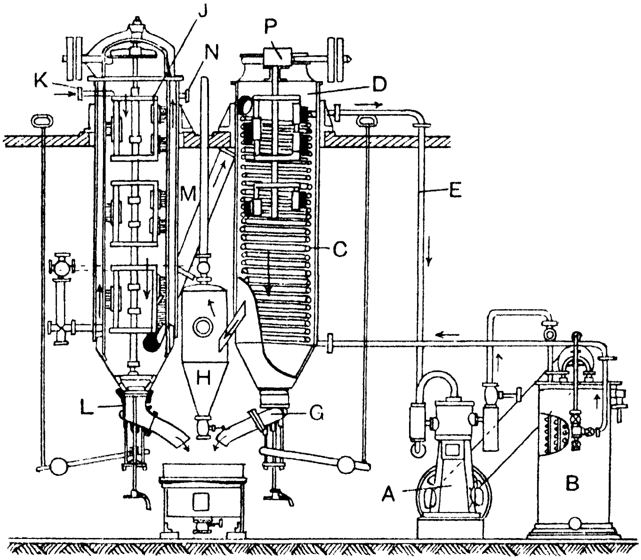


FIG. 3.—Passburg Crystalliser.

The crystallisers described above operate intermittently and are sometimes designated batch crystallisers, but there are others, which, still adopting the principle of cooling the solution, operate continuously.

Sometimes crystallisers belonging to this group consist of a trough having a semi-cylindrical base and fitted with a spiral agitator mounted on and driven by a shaft the axis of which coincides with the axis of the trough. In another type of uncontrolled crystalliser the hot concentrated solution is run into a shallow, rectangular tray. Dipping into this tray is a hollow cylinder with its axis horizontal. Through the trunnions supporting this cylinder pass pipes for the admission and removal of the cooling liquid. By means of a ball-valve the hot concentrated solution in the tray is kept at such a level that the rotation of the drum causes its outer surface to be covered by a thin film of liquid from the tray. Contact with this cooled surface causes the crystals to form on the surface of the drum from which they are removed by scrapers or doctors placed as shown in Fig. 4, which gives an end view of the film or dipping drum type of crystalliser which is continuous in operation. The examples given illustrate the main features of crystallising plants for uncontrolled crystallisation by cooling.

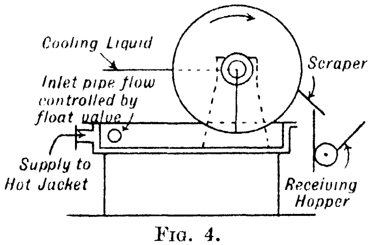


FIG. 4.

Another continuous crystalliser employing this principle is represented by the Swenson-Walker crystalliser, Fig. 5, which consists of an open trough having a semi-cylindrical base and placed with its axis horizontal. The axis of the trough coincides with the axis of a shaft B, which extends the whole length of the trough and carries the worm or ribbon conveyor C, being driven by means of a worm and worm wheel D supported on the end at which the hot solution is admitted. Surrounding the lower portion of the trough is a jacket E through which the cooling liquid can circulate. These crystallisers are usually made in sections 10 ft. long, four sections being bolted together to produce a trough 40 ft. in length. The outlet F of the jacket of one section is connected by an inverted U-tube, G, to the inlet of the next section, H, the process being repeated until all the jackets are connected in series. Counter-current flow of the hot solution and the cooling liquid is thus assured. The end plate of the last section is fitted with a weir, K, over which the cooled liquid and crystals flow, either into a centrifugal machine if crystallisation has been completed or in series through one or more similar crystallisers if further cooling is desired before the solution and crystals formed are finally separated usually by centrifuging. A variant of this type of crystalliser sometimes adopted is a long tube which is mounted and driven in a similar manner to a tube mill. The hot solution enters at one end and the cooled solution leaves at the other, a stationary screw conveyor or plates arranged spirally on the inner surface of the tube being employed to move the crystals to the outlet end.

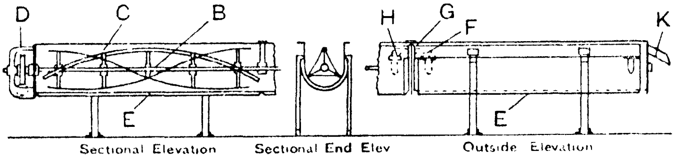


FIG. 5.—First and Last Sections of Swenson-Walker Crystalliser.

Rotating conveyors in these crystallisers unless carefully adjusted are liable to break a number of the crystals thus forming additional nuclei and so give an output of crystals of varying sizes.

In an attempt to reduce this attrition of the crystals to a minimum and so produce a uniform product, the Wulff and Bock or rocking crystalliser has been developed.

Such a machine consists of a long trough up to 100 ft. in length and supported so that its axis is slightly inclined to the horizontal. Fig. 6 represents a view of such a crystalliser and shows the rockers or rings, the rollers which support them, and the bracing between the trough and the rockers and each pair of rockers. The trough is designed so that as it is rocked to and fro the solution will not be ejected over the edges and is fitted with a series of transverse vertical baffle plates which divide the length of the trough into a series of compartments. As these partitions do not extend across the trough, but are arranged to provide openings alternately on the right and left hand sides of the trough the solution, which is admitted at the highest point, in its passage through the crystalliser must follow a sinuous path before it reaches the outlet placed in the lower end plate.

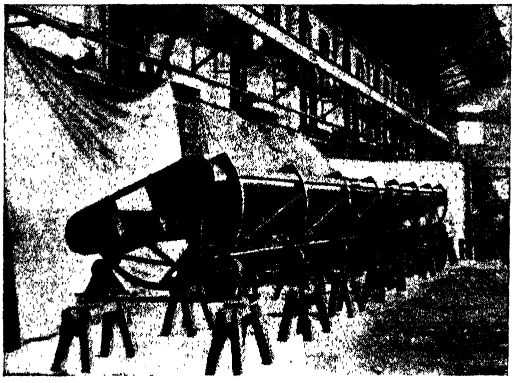


FIG. 6.—Wulff and Bock Crystalliser.

Rocking of these crystallisers is effected by suitably controlled hydraulic rams or by electrically driven rocking gear. Special attention should be given to the strength of the machine because at the points of reversal of rotation large stresses can be set up in the structure.

Another crystalliser in which crystallisation is effected by cooling a saturated solution whilst in motion is the Howard Crystalliser, of which Fig. 7 represents a diagrammatic view. This apparatus is formed of three truncated conical vessels placed one above the other and having their axes in line. The lower two vessels are provided with jackets, whilst in the upper vessel there is a coiled tube. The saturated solution is admitted to the lowest vessel B through the pipe A, and after filling this vessel rises into the middle vessel D through the short tube C.

Inside this vessel is another conical chamber, E, within which is a pipe, for the removal of cooling liquid, which extends nearly to the bottom of this vessel. The taper of this conical vessel is such that in the ascent of vessel D the sectional area of the annulus formed by these two vessels continually increases. In this way the velocity of the liquid rising in vessel D is being continually reduced and so only crystals of a definite size are capable of falling into the vessel B. Cooling liquid is admitted to the jacket of vessel D at F, and removed at G, whilst the cooling liquid for vessel E is admitted at H and removed at K. On reaching the top section, L, crystal growth is stopped by circulating a hot liquid through the coils which heats the surrounding liquid before it flows over the weir fixed at the top of this vessel and so reaches the outlet M. Hot liquid is also circulated through the jacket of vessel B, entering at N and leaving at P, and this maintains the temperature of the liquid in B at such a point that no further growth can take place on the crystals in this vessel. The lower end of B is connected to a salt box or boot of an elevator by which the crystals can be removed from the plant.

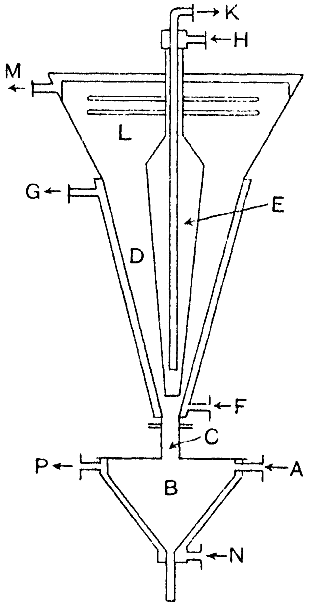


FIG. 7.—Howard Crystalliser.

Formation of crystals by hot solutions can also be effected by forcing the solution in the form of a fine spray into a cooling tower or by making the solution fall in the form of drops through a current of cold gas or air which is drawn through a duct (" Der Chemie Ingenieur," vol. 1, part III, pp. 203, 204).

CRYSTALLISATION BY EVAPORATION.

An early type of plant for this purpose resembles the tank crystalliser used for uncontrolled crystallisation by cooling, but in this case the tank is arranged in a brickwork setting so that hot gases from a furnace placed in the setting at one end of the tank can pass over the walls and bottom of the tank and heat its contents. Sometimes these tanks are provided with a series of parallel tubes placed near the bottom of the tank and fixed between the end plates of the tank through which the hot gases from the furnace, placed at one end of the tank can pass on their way to the chimney. During both the cooling and evaporating methods employed in crystallising pans, vapour is evolved at the free surface of the liquid and if still air conditions are maintained, above the pan, the following formula, devised by J. W. Hinchley, enables the rate of evaporation of the solution to be determined :

$$W = A\left(\frac{p_e - p_d}{50}\right)^{1\cdot 2}$$

where W = weight of liquid evaporated in kilograms per hour per sq. metre of surface of the liquid; p_e = vapour pressure of the solution in mm. of mercury at the temperature under consideration; p_d = pressure of the aqueous vapour in the atmosphere of the factory; and A = constant, depending on the solution undergoing evaporation.

If air currents are directed over the free surface of the liquid then the work by Hinchley and Himus (Trans. Inst. Chem. Eng. 1924, **2**, 57) and other workers (Himus, *ibid.* 1929, **7**, 166; Powell and Griffiths, *ibid.* 1935, **13**, 175) shows how the evaporation can be determined for a given set of conditions. With this type of crystalliser the movement of the liquid is largely due to convection currents, and therefore the growth of small crystals, which are retained at the free surface by the surface tension of the liquid, will not occur in a regular manner.

Evaporators can be used to concentrate the solution, which may then pass into a cooler, or a vacuum pan, where the crystallisation is carried out, or the arrangement may be such that the crystals are formed in the evaporator or separator of the plant and are subsequently withdrawn after the removal of the surplus mother liquor. Usually the latter type of plant is referred to as a *salting evaporator* and has a special field in the production of fine-grained crystals.

When evaporators are used to concentrate the solution either for the coolers or vacuum pans any of the different types of heating may be employed, but in the salting evaporators vertical tubes are used in the heating element. The commonest forms, are a series of vertical tubes extending between two tube plates with a large central downcomer, the basket type of heater, and the individual heater or calandria of the climbing film type. In the first two types the lower cover attached to the evaporator shell is conical and its lowest point connected with the device for removing the crystals. Sometimes when a central downcomer is employed forced circulation of the liquor in the evaporator is produced by means of a propeller placed at or near the bottom of this tube. In the conical base below the heaters is a region in which the solution is comparatively quiescent and in which growth of crystals can proceed until they are able to fall into the receiver. When a separate calandria or heater is employed the hot liquor has to be discharged into a separator where the vapour produced during its passage through the heater or generated from the superheated liquor by the reduction in pressure, is separated from the liquor. At the bottom of this separator means are provided for the recovery and removal of the crystals produced and the return of the liquid to the calandria for further heating.

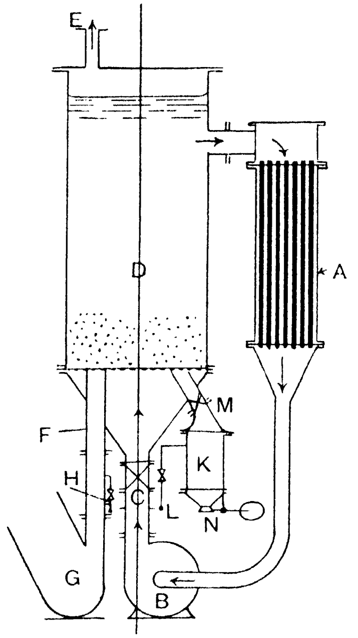


Fig. 8.—Borske Saltverker Crystalliser.

An important development in the subject of crystallisation by evaporation was published in Chem. Trade J. and C. Eng. Jan. 16, 1925, when a crystalliser developed by the A. S. de Borske Saltverker of Bergen for the production of coarse-grained salt for fishery work was described.

Fig. 8 illustrates diagrammatically the early form of this crystalliser. In this arrangement of the plant the solution is drawn through the heater A by the pump B and forced through the valve C into the bottom of the chamber D. At the bottom of this chamber is a perforated plate upon which a quantity of crystals have been placed. During its passage through the heater the liquid becomes superheated due to increased pressure produced by the increase in the head of the liquid and no vapour is generated until it is near to the free surface of the liquid in D. If the solution is saturated the evolution of vapour, which escapes through E, causes the remainder of the liquid to become supersaturated. Part of this again passes through the heater and is again superheated, the cycle being thus continuous. Thus the crystals on the perforated plate are always in contact with a supersaturated solution and will increase in size. Moreover, the liquid from the centrifugal moving upwards will keep these in suspension until they attain such dimensions that they can overcome the upthrust of the rising liquid, when they will fall into the tube F connected with the shoe of the bucket elevator G, by which they are removed from the crystalliser. Liquid is fed continuously to the crystalliser through the pipe H, and by adjusting the valves on the pipe H and the discharge from the centrifugal pump C, the upward flow of liquid in the pipe F and through the perforated plate can be regulated so that only crystals of a definite size fall into the shoe of the elevator.

An alternative method of removing the crystals, employing crystal boxes, is shown at K. If desired several of these can be arranged so as to remove the crystal from several points round the perforated plate. Here again the feed which is admitted by the pipe L provides the upward flow which regulates the size of crystal entering the box. When several boxes are employed, then by closing the feed valve and the valve M and opening the valve N the crystals can be discharged from each box in turn and thus produce the minimum disturbance in the running of the plant.

The bucket elevator and the crystal box are two common methods of removing the crystals from salting evaporators. When the bucket elevator is used the casing enclosing the buckets must be liquid-tight and must extend to such a height that the hydrostatic pressure produced by the head of cool liquid above the bottom of the shoe will always be equal to the pressure on the free surface of the liquid plus the pressure due to the height of the hot liquid measured from the same datum level. Two or more crystal boxes are usually provided, so that whilst one is being emptied of its crystals the crystals which are being formed can collect in the others.

A modified form of the crystalliser shown in Fig. 8 is the Jeremiassen or Oslo crystalliser (J. H. Perry, "Chemical Engineering Handbook," 1934, 1484), Fig. 9. In this plant the liquid, after being superheated in its downward passage through the heater A is forced by the centrifugal pump B into the vessel C, where evaporation takes place as the result of the reduction in pressure.

Removal of solvent from a saturated solution at this point results in the solution becoming supersaturated and this falls by the pipe D into the crystalliser E. As the lower end of the pipe D passes through a perforated plate fixed near the bottom of the crystalliser and upon which the seed crystals are supported, the supersaturated solution discharged by D must by its upward passage through the plate maintain the crystals thereon in suspension until they attain such dimensions that they can fall against the ascending stream on to the perforated plate. On opening the valve G these crystals enter the crystal box F, and can be withdrawn from the crystalliser whilst the solution rising to the top of the crystalliser again is superheated by passing through the heater A. Liquid is supplied to the crystalliser through the pipe H, the feed being either of a continuous or intermittent nature.

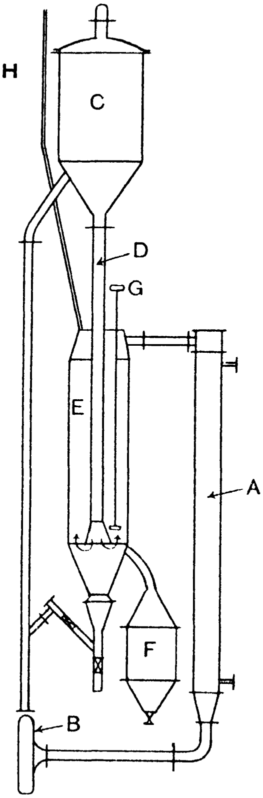


Fig. 9.—Jeremiassen or Oslo Crystalliser.

Crystallisation under Reduced Pressure.

In some industries, notably the sugar industry, the concentrated liquid is pumped into a vacuum pan where the final water is evaporated under reduced pressure and the crystal formation effected.

Vacuum pans closely resemble evaporators, the heating elements being either coils or one of the various types of tubular heaters. Syrup fed to these vacuum pans has a high viscosity, so that it becomes practically impossible for the crystal of sugar to settle in the liquor and therefore special attention must be given to maintaining good circulation of the liquid in the pan.

When coils are used for heating the liquid the spacing between the top coils should be greatest and gradually diminish in the lower layers. Heaters having large vertical tubes also materially assist circulation, whilst an essential feature of such pans is a downcomer of ample cross-sectional area.

Another important factor in operating such pans is the vacuum, for it is generally conceded that a high vacuum results in crystals of soft grain whilst hard grain crystals are obtained if a low vacuum is employed. Usually in the sugar industry the working pressure in the vapour space of the vacuum pan is below $3\frac{1}{2}$ lb. per sq. in. absolute. If the viscosity of the saturated solution is low, then in crystallisers of this type small crystals are produced because the crystal once formed tends to sink rapidly through the solution. To produce large crystals in such a plant the problem is largely to maintain these small crystals in contact with the supersaturated solution for sufficient time to allow of their growth to the size required.

In the vacuum crystalliser, however, another principle is involved. If a saturated solution at a temperature corresponding to its boiling-point at atmospheric or higher pressure is admitted to a vessel within which there is a lower pressure, the solution will be at a higher temperature than a similar solution boiling at the lower pressure This superheated liquid will fall in temperature to the boiling-point of the liquid at the lower pressure and the heat thus rendered available will cause some of the solvent to vaporise. The remainder of the solution will therefore become supersaturated and crystallisation or crystal growth will occur. Such a method cools the solution without transferring the heat to be dissipated through the walls of the container, and can be used for cooling nearly all aqueous solutions and many solutions in which organic solvents are employed. Condensation of the vapour evolved in a suitable condenser maintains the requisite pressure in the crystalliser and allows the solvent to be recovered. This is particularly advantageous when organic solvents are employed, especially in large-scale operations. Fig. 10 (Griffiths, Chem. Eng. Group Proc. 1924, **6b**, 9) illustrates a vacuum crystalliser of the rocker type, the hot saturated solution being admitted by a pipe passing through the end plate at the higher end, whilst the cooled solution together with the crystals are removed through suitable openings in the lower end plate. Connections are also provided on this plate for the removal of the vapour evolved.

Another vacuum crystalliser (Badger and McCabe, " Elements of Chemical Engineering," 1931, p. 418) is shown diagrammatically in Fig. 11. Here the hot saturated solution enters at A into the vessel B in which the pressure is less than atmospheric and as a result an amount of vapour is evolved which is removed through C to the condenser or vacuum pump by which the reduced pressure in B is maintained. The supersaturated solution thus formed permits of crystal growth and the rapid evolution of vapour from the entering solution keeps the liquid in the bottom of B sufficiently agitated that a certain amount of growth must occur before the crystals are capable of falling through the barometric leg D and into the vessel E. All the time that the crystals are descending the tube D, they remain in contact with the supersaturated solution. On reaching the bottom of E the solution and crystals are transferred by the pump F to the settler G, and from thence to one or other of the centrifugal machines H for final separation of the crystals from the mother liquor. The overflow from the settler and the discharge from the centrifugals are returned to the vessel E, which is provided with an outlet K for mother liquor free from crystals.

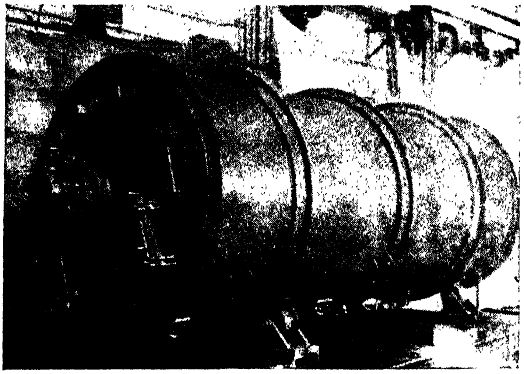


FIG. 10.

OTHER METHODS.

Since crystal formation depends upon first, either the formation of nuclei or the addition of small seed crystals to the solution and, secondly, keeping the concentration of the solution at the working temperature in the metastable region if crystal size is the object or in the supersaturated region if fine crystals of varying sizes are desired, any method such as the adsorption of the solvent or the addition of some material to the mother liquor which diminishes the solubility of the substance, which it is desired to crystallise, in the solvent are means by which crystal formation can be effected. The addition of impurities to the mother liquor, however, even in small quantities affects materially both the rate of crystal formation and the rate of crystal growth.

As impurities inhibit the growth it is usual therefore in industrial practice to prefer one or other of the three methods outlined above as the principle upon which the crystalliser operates, rather than by introducing impurities to change the solubility of the dissolved material in the solvent.

CONDITIONS DURING CRYSTAL GROWTH

If the rate at which the material is deposited on the faces of the crystal is to be kept constant, it is necessary to maintain the same concentration of the mother liquor so the rate of evaporation or rate of cooling or both must be progressively increased as the crystals grow in size.

Let d_1=mean dimension of the small crystals; d_2=mean dimension of the larger crystals grown from the smaller; n=number of faces on each crystal; N=number of crystals under consideration; S_1=total surface of the small crystals; S_2=total surface of the large crystals; w=weight of material crystallised per unit area of surface per unit time.

With controlled crystallisation the crystals increase in size but not in number, so that N is constant. The mean dimensions of the crystals are such that nd_1^2 equals the surface of one of the small crystals and nd_2^2 the surface of the large crystal.

Total surface of small crystals $=S_1=Nd_1^2n$.

Total surface of large crystals $=S_2=Nd_2^2n$.

Weight of material removed per unit time by small crystals $=wNd_1^2n$.

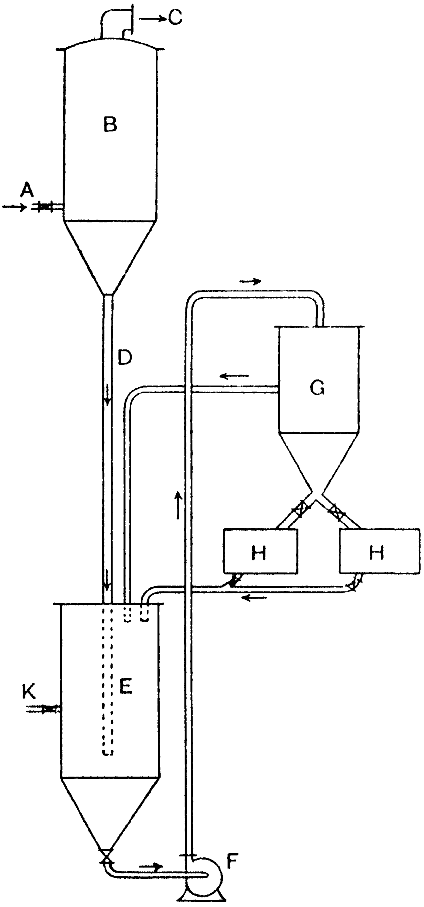


FIG. 11.

Weight of material removed per unit time by large crystals = wNd_2^2n.

This shows that for a constant rate of deposition on the crystal surface much more material will be removed from the solution by large crystals than by small crystals in the same time; therefore the rate of cooling or the rate of evaporation or both must be progressively increased with the size of the crystal if the concentration of the solution is not to fall rapidly to the saturation line when further growth becomes impossible.

S. G. M. U.

CRYSTOLON (CARBORUNDUM) *v.* ABRASIVES.

CUBANITE. A copper ore with the composition $CuFe_2S_3$ (Cu 23·4%). It is usually massive with a brass-yellow or bronze-yellow colour and intimately intergrown with chalcopyrite, pyrrhotine, etc. Sp.gr. 4·1, hardness 3½. The mineral was first described by A. Breithaupt in 1843 from Barracanao in Cuba (hence the name), and soon afterwards recognised from Tunaberg in Sweden. It was long regarded as a rare mineral, supposed to be cubic in crystallisation, until polished sections of ores came to be examined by the metallographic method, when it was found to be of wide distribution. It was also found to be anisotropic, and therefore not cubic, and was identified with the small orthorhombic crystals of the same composition from the Morro Velho gold mine in Brazil, which E. Hussak in 1902 named *chalmersite*. Larger crystals have since been found at Sudbury in Canada (M. A. Peacock and G. M. Yatsevitch, Amer. Min. 1936, **21**, 55).

L. J. S.

CUBEBOL. The sesquiterpene alcohol, *cubebol*, $C_{15}H_{26}O$, m.p. 61–62°, occurs in oil of cubebs (Henderson and Robertson, J.C.S. 1930, 1908). It yields a *phenylurethane*, m.p. 186° and an *α-naphthylurethane*, m.p. 197–198·5°. Its structure has not been determined and it does not appear to be identical with cubeb-camphor examined by Blanchet and Sell, (Annalen, 1833, **6**, 294).

J. L. S.

CUBEBS, ESSENTIAL OIL OF. The oil distilled from the dried, full-grown, unripe fruits of *Piper cubeba* Linn. (Fam. Piperaceæ), a tree indigenous to the Malay Archipelago, chiefly Java and Singapore; yield 10–15%. Other piperaceous fruits resembling cubebs are sometimes found in commerce.

Constituents.—Pinene, dipentene, and cadinene have been detected, and a sesquiterpene alcohol cubeb-camphor (m.p. 67°), which is sometimes separated from old oils. The blue colour is probably due to the presence of azulene.

Characters.—A greenish or greenish-blue oil, sp.gr. 0·910 to 0·930, optical rotation −25° to −40°, ref. ind. 1·486–1·500. Soluble in 10 volumes of 90% alcohol.

C. T. B.

CUCUMBER. The fruit of *Cucumis sativus* Linn. The composition of the cucumber varies particularly with size and with growth conditions, notably the level of supply of nitrogen to the roots (Dearborn, Cornell Agric. Exp. Sta. Mem. 1936, No. 192). Heinze (Z. Nahr.-Genussm. 1903, **6**, 529, 577) records the following analyses:

	Water.	Protein.	Fat.	Glucose.	Cane sugar.	Other carbohydrates.	Fibre.	Ash.
	%	%	%	%	%	%	%	%
Small	96·6	0·81	0·09	0·00	0·10	1·44	0·58	0·34
Large	95·8	0·67	0·09	0·66	0·09	1·60	1·65	0·42

Dearborn (*l.c.*) shows the composition of the whole plants on a somewhat different basis (as percentage of dry matter):

	Stems.	Leaves.	Fruits.
	%	%	%
Soluble solids	23·6–26·7	15·2–22·8	58·9–58·3
Soluble **N**	0·212–0·562	0·151–0·365	0·304–0·710
Insoluble **N**	0·794–1·349	1·50–2·97	0·961–0·994
Amino-**N**	0·050–0·098	0·025–0·073	0·102–0·245
Amide-**N**	0·019–0·020	0·011–0·020	0·030–0·049
Nitrate-**N**	0·026–0·250	0·018–0·077	0·034–0·021
Lipin-**N**	0·003–0·000	0·027–0·064	0·004–0·041
Residual **N**	0·014–0·193	0·074–0·139	0·133–0·252
Reducing sugars	8·12–4·15	1·36–1·95	47·9–45·1
Non-reducing sugars	1·10–1·23	0·12–0·10	0·29–0·00
Starch	6·81–4·58	2·25–0·34	1·61–1·72
Acid-hydrolysable polysaccharides	2·99–2·89	12·01–4·81	2·79–2·65

Of the two figures given for each value the first refers to plants grown with a restricted, and the second to those grown with a generous, supply of nitrogen in the soil. According to M. Kitahara (J. Agric. Chem. Soc. Japan, 1936, **12**, 595) the principal sugars are glucose and fructose. In hot water extracts of the fruit Yoshimura and Nishida (J. Chem. Soc. Japan, 1924, **45**, 49) found adenine, trigonelline, and arginine.

Analysis of cucumber seeds is reported by Einhorn *et al.* (Maslob. Shir. Delo. 1929, **45**, 44) as water 8·0, protein 29·7, fat 31·5, sugars, starch, etc. 1·9, pentosans 4·7, cellulose 13·9, pectins 0·6, phytin 1·1, lecithin 2·6, ash 3·9, P_2O_5 2·25%. The oil contains fatty acids, comprising stearic acid 3·72, palmitic acid 6·8, oleic acid 58·5, linolic acid 22·3%, and exhibits the following characteristics: d_{15} 0·9251, ref. ind. 1·4761 (25°), solidifying pt. −3·5°, saponification value 191·1, iodine value 115·3, Reichert-Meissl value 0·5–1·05, Polenske value 0·87, acetyl value 16·6, acid value 3·5–10·7.

The composition of the ash of cucumbers varies considerably with the manner and locality in which they are grown. The following data are representative values :

K_2O	Na_2O	CaO	MgO	Fe_2O_3
%	%	%	%	%
38·51	4·95	6·4–7·0	3·2–4·5	0·8

P_2O_5	SO_3	SiO_2	Cl
%	%	%	%
13–19	5·5–6·5	4·2–8·0	6·4–9·2

Small proportions of manganese, copper, and zinc are also recorded by various analysts.

A. G. Po.

CUDBEAR. A purplish-red powder employed as a colouring agent, obtained by digesting *Rocella* lichen with ammonia.

CULLEN EARTH or COLOGNE EARTH. A variety of brown coal or lignite, of limited use as a pigment.

CUMENES, C_9H_{12}. The name cumene, originally given to *iso*propylbenzene to indicate its connection with cumic acid, from which it was obtained by distillation with lime, is frequently used as a generic term including any of the isomeric benzene hydrocarbons of the formula C_9H_{12}. Theory predicts the existence of eight of these, all of which have been found in coal tar oil.

Propylbenzenes.—(1) NORMAL PROPYLBENZENE (*n*-cumene), $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$. *n*-Propylbenzene may be obtained by the general methods applicable to the formation of alkyl benzenes. It is conveniently prepared (70–75% yield) by the action of diethyl sulphate on an ethereal solution of $PhCH_2Cl$ ("Organic Synthesis," New York, 1925, vol. 4, p. 59).

Allyl *cyclo*hexane with platinised charcoal at 200°C. is converted to a mixture of propyl*cyclo*hexane and propylbenzene (Levina and Tzurikov, J. Gen. Chem. Russ. 1934, **4**, 1250). The equilibrium :

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3+3H_2 \rightleftharpoons C_6H_{11}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

in the presence of a-palladium catalyst has been investigated (*ibid.* 1933, **3**, 718).

Propylbenzene (b.p. 157°) has normal aromatic reactivity. Also it is interesting that it reacts with carbon tetrabromide giving $C_6H_5{\cdot}CHBr{\cdot}C_2H_5$ (Hunter and Edgar, J. Amer. Chem. Soc. 1932, **54**, 2025), and with chromyl chloride, giving a double compound that on decomposition with water yields benzyl methyl ketone (von Miller and Rohde, Ber. 1890, **23**, 1070). Vigorous oxidation converts propylbenzene to benzoic acid. A number of papers on the nitration of alkyl benzenes studied from the point of view of modern electronic theories have recently appeared in the Journal of the Chemical Society : *p-iso*propyltoluene—Le Févre, 1933, 980; *p*-ethyltoluene—Brady and Day, 1934, 114; *n*-propylbenzene—Brady and Cunningham, 1934, 121; *p-tert*-butyltoluene—Brady and Lahiri, 1934, 1954.

(2) *iso*PROPYLBENZENE (CUMENE).—*Formation.* Cumene may be synthesised by many general methods. It may be prepared by the action of *iso*propyl sulphate on phenyl magnesium bromide (Bert, Compt. rend. 1923, **176**, 840), by condensation of *iso*propyl alcohol and benzene in the presence of concentrated sulphuric acid (Meyer, Monatsch. 1929, **53**, **54**, 721) and by condensation of *iso*propyl chloride and benzene in the presence of a little aluminium chloride (Radziewanowski, Ber., 1895, **28** 1137). It is also readily obtained by boiling 1 part of *p*-cymene, 10 parts of benzene, and 0·05 part of aluminium chloride for 10 hours, washing with water and fractionating (Bœdtker and Halse, Bull. Soc. Chim. 1916, [iv], **19**, 447) :

$$C_6H_4MePr^{\beta}+C_6H_6 \rightarrow C_6H_5Me+C_6H_5Pr^{\beta}.$$

Cumene is formed with other propyl benzenes by the alkylation of benzene with propylene using various catalysts, *e.g.* H_2SO_4 or H_3PO_4 (U.S.P. 2006541) or BF_3 (Nieuwland *et al.*, J. Amer. Chem. Soc. 1935, **59**, 1547). Cumene is produced when the vapours of certain terpenes are passed over heated metals (**Ni, Cu**) (Sabatier *et al.*, Compt. rend. 1919, **168**, 671; 1919, **162**, 929). It occurs in coal tar (Schultz, Ber. 1910, **43**, 2517) and in American petroleum (Mabery and Dunn, Amer. Chem. J. 1896, **18**, 215). The preparation of cumene from propyl bromide, benzene, and aluminium chloride, and that of cymene from *p*-bromotoluene, normal propyl bromide, and sodium (Fittig, Schäfer, and König, Annalen, 1869, **149**, 331) was for a long time the cause of great confusion in ascertaining the constitution of members of the cumene and cymene groups, as it was not realised that in each case the propyl- group changed into the *iso*propyl- group owing to the temperature of the reaction not being regulated.

Cumene has b.p. 152·6°–152·8°/759 mm., d_4^{20} 0·862. With *tert*-butyl alcohol and concentrated sulphuric acid cumene yields *tert*-butylcumene (H. Barbier, 14ième Congrès de Chimie Industrielle, Paris, Oct. 1934). Vigorous oxidation of cumene yields benzoic acid. With chromic acid or permanganate in glacial acetic acid, phenyl dimethyl carbinol is produced (Bœdtker, Bull. Soc. Chim. 1901, [iii], **25**, 846). Cumene reacts with chromyl chloride in carbon disulphide solution, giving an addition compound which on decomposition with water gives hydratropic aldehyde, $C_6H_5{\cdot}CHMe{\cdot}CHO$, and acetophenone (von Miller and Rohde, Ber. 1891, **24**, 1357). Dilute nitric acid (*d* 1·075) in a sealed tube at 105°C. reacts with cumene, giving *β*-nitro-*β*-phenylpropane (Konowalow, Ber. 1894, **27**, 468; 1895, **28**, 1856).

Cumene may be nitrated and sulphonated in the usual way (Gibson, J.C.S. 1920, **117**, 948; Bert and Dorier, Bull. Soc. chim. 1927, **41**, 1170.) Chlorination of cumene yields mono-, di-, tri-tetra-, and penta-chloro cumenes and the corresponding chlorobenzenes. The *iso*propyl group is thus easily displaced. On nitration of tri-, tetra-, and penta-chlorocumenes, the *iso*propyl group is replaced by the nitro group (Qvist and Salo, Chem. Zentr. 1934, **2**, 594). Propyl chloride, *tert*-butylbenzene, and *p-di-tert-*

butylbenzene are formed from cumene, *iso*butyl chloride and a very little aluminium chloride at room temperature (Bœdtker, Bull. Soc. chim. 1906, [iii], **35**, 834).

(3) **Methylethylbenzenes.**—The methylethylbenzenes, prepared by the action of sodium on a mixture of ethyl bromide or iodide with the corresponding bromo-toluenes, are liquids with boiling-points—*o*-, 158–159°, *m*- 158–159°, *p*- 161·2°, and specific gravities of approximately 0·87 at 16°C.

Trimethylbenzenes.—(1) *Consecutive trimethylbenzene* (hemimellitene, hemimellitrine), $C_6H_3(CH_3)_3$ (1:2:3) is obtained by heating *a*-*iso*duric acid $C_6H_2(CH_3)_3CO_2H$ with lime. It has recently been isolated from an Oklahoma petrol (Beveridge and Schicktanz, J. Res. Nat. Bur. Stand. 1933, **2**, 665). The benzenoid hydrocarbons of the fraction, b.p. 118–132°/215 mm., were separated from other hydrocarbons by extraction with liquid sulphur dioxide and from one another by processes involving distillation, crystallisation, selective sulphonation, crystallisation of the sulphonic acids, and selective hydrolysis of the sulphonic acids. It was estimated that mesitylene, pseudocumene and hemimellitene are present in the crude petroleum used in the proportions 0·02, 0·2, and 0·06% respectively.

Hemimellitine has b.p. 176·1, sp.gr. 0·8951 (20°C.), n_D^{25} = 1·5116.

(2) *Unsymmetrical trimethylbenzene* (*ψ-cumene*), $C_6H_3(CH_3)_3$ (1:2:4), occurs together with mesitylene in coal-tar (Beilstein and Kögler, Annalen, 1866, **137**, 317), and is present in many petroleums (Poni, Chem. Zentr. 1906, **1**, 459). It is prepared by the action of sodium on a mixture of either bromo-*para*xylene or bromo-*meta*xylene with methyl iodide. In order to isolate it from coal tar, Armstrong recommends (Chem. News, 1878, **38**, 5; Ber. 1878, **11**, 1697) that the mixture of *ψ*-cumene and mesitylene (*v. infra*) boiling between 160° and 170°, obtained from coal tar by fractional distillation, should be converted into their sulphonic acids, and the mixture heated with concentrated hydrochloric acid in a sealed tube for 1 hour at 100°. In this way the mesitylenesulphonic acid is decomposed, regenerating mesitylene, whilst the *ψ*-cumenesulphonic acid is not attacked. After separating the mesitylene the *ψ*-cumenesulphonic acid is precipitated from the hydrochloric acid solution by sulphuric acid, purified by recrystallisation from dilute sulphuric acid, and finally decomposed by heating with hydrochloric acid at 140–150°, when it breaks up into *ψ*-cumene and sulphuric acid. A slight modification of this method of separation is described by Smith and Cass, J. Amer. Chem. Soc. 1932, **54**, 1603). Jacobsen (Ber. 1876, **9**, 256) separates the two isomeric sulphonamides by recrystallisation from alcohol, in which mesitylenesulphonamide is readily, *ψ*-cumenesulphonamide only sparingly, soluble. The sulphonamides are then hydrolysed by heating with concentrated hydrochloric acid at 175°.

Another method proposed by Jacobsen (Annalen, 1877, **184**, 199) is to separate the two sulphonic acids by fractional crystallisation; *ψ*-cumenesulphonic acid is soluble with difficulty in sulphuric acid and crystallises out. On heating to its melting-point (110°) and passing in steam at a temperature of 250°, pure *ψ*-cumene is obtained (*see also* Schultz and Herzfeld, Ber. 1909, **42**, 3602). *ψ*-Cumene boils at 168·2°, and has sp.gr. 0·877 at 18° (Schultz and Herzfeld, *l.c.*). On oxidation with nitric acid, it yields two isomeric acids of the formula $C_6H_3(CH_3)_2CO_2H$—xylic acid and *p*-xylic acid—and a small quantity of the isomeric methyl*iso*phthalic and methylterephthalic acids:

$$C_6H_3(CH_3)(CO_2H)_2$$

(Bentley and Perkin, J.C.S. 1897, **71**, 165).

Oxidation of *ψ*-cumene with lead dioxide or manganese dioxide in the presence of sulphuric acid or electrolytically yields considerable quantities of 2:4-dimethylbenzaldehyde (Perkin and Law, J.C.S. 1907, **91**, 263, 752). When boiled with aluminium chloride *ψ*-cumene is converted to a mixture of benzene, toluene, xylene, mesitylene, durene, etc. (Jacobsen, Ber. 1885, **18**, 341; Anschütz, Annalen, 1886, **235**, 186). This is a general type of reaction for polymethylbenzenes.

(3) *Symmetrical Trimethylbenzene* (mesitylene), $C_6H_3(CH_3)_3$ (1:3:5).—Mesitylene occurs in the coal tar fraction of b.p. 157–162° (Fittig and Wackenroder, Annalen, 1869, **151**, 292; Schultz, Ber. 1909, **42**, 3602), and in American petroleum. It is obtained on elimination of 3 molecules of water from 3 molecules of acetone. This elimination may be brought about by means of sulphuric acid (Organic Syntheses, **2**, 41).

Mesitylene is formed on dissolving allylene, $CH_3{\cdot}C\vdots CH$ in sulphuric acid and distilling with water (Fittig and Schrohe, Ber. 1875, **8**, 17). Mesitylene has b.p. 164·5, sp.gr. 0·8768 4°/4°. It has the normal reactivity of a compound of its constitution.

CUMIDINES, $C_9H_{13}N$. The term "cumidine," which originally was proposed for the monobasic derivatives of cumene (*iso*propylbenzene) includes also by accepted usage numerous basic derivatives of pseudo- or (*ψ*)-cumene (1:2:4-trimethylbenzene, mesitylene (sym. trimethylbenzene), *n*-propylbenzene, and other bases of the same empirical formula. Of these isomers only those of practical interest are treated below, the most important being sym-*ψ*-cumidine and mesidine.

***ortho*Cumidine,** *o*-amino*iso*propylbenzene, is formed by decarboxylation of aminocuminic acid with baryta (Cahours, Annalen, 1859, **109**, 19) and to a smaller extent by reduction of the crude nitration product of cumene. It yields normal salts and has b.p. 213·5–214·5/732 mm. Passage over hot lead peroxide yields indole. The acetyl derivative has m.p. 72°.

Cumidine, *p*-amino*iso*propylbenzene, is made by nitration of cumene with fuming nitric acid and reduction of the nitrocompound with ammonium sulphide (Constam and Goldschmidt, Ber. 1888, **21**, 1157) and also by direct condensation of aniline with *iso*propyl alcohol in presence of zinc chloride at 260° (Louis, Ber.

1883, **16**, 111). B.p. 216–218°, acetyl derivative m.p. 102–102·5°. On oxidation with sodium chlorate and potassium ferrocyanide in hydrochloric acid solution, cumidine yields an "aniline-black" dyestuff (Kirpitschnikow, Chem. Zentr. 1906, **1**, 829) and it is also the source of a dyestuff obtained by condensation with cyanogen chloride in pyridine solution (G.P. 155782).

***para*Aminopropylbenzene** is formed by condensation of aniline with propyl alcohol (Willgerodt and Sekerl, Annalen, 1903, **327**, 301) and has b.p. 224–226°, acetyl derivative, m.p. 96° (for preparation, *see* G. Baddeley and J. Kenner, J.C.S. 1935, 303).

Mesidine, obtained by reducing nitromesitylene with tin and acid (Fittig and Storer, Annalen, 1868, **147**, 3) as well as by numerous less usual methods of introducing an amino group, has b.p. 229°, acetyl derivative, m.p. 216°. Mesidine undergoes normal reactions and finds some use as a dye intermediate.

ψ-Cumidine, sym.-ψ-cumidine

$$(CH_3{:}CH_3{:}CH_3{:}NH_2 \cdot 1{:}2{:}4{:}3)$$

is obtained by reducing nitropseudocumene with tin and hydrochloric acid, but is more economically prepared by digesting technical xylidine with methyl alcohol at 300°, the basic mixture being separated by crystallisation of the nitrates (G.P. 22265). ψ-Cumidine has m.p. 63°, b.p. 234°, is insoluble in water and is characterised by a sparingly soluble nitrate and by complexes with sym-trinitrobenzene and sym-trinitrotoluene (Noelting and Sommerhoff, Ber. 1906, **39**, 78); acetyl derivative, m.p. 161°. ψ-cumidine while exhibiting many normal reactions undergoes some remarkable condensations and oxidations to substituted acridines (Senier and Compton, J.C.S. 1907, **91**, 1934) and hydroquinolines (Jones and White, *ibid.* 1910, **97**, 643). Reaction with α-bromo*iso*valeryl bromide yields a hypnotic **N**-alkyl derivative, but ψ-cumidine is more important as the source of azo-colours of the Ponceau series (Schultz, Tab. No. 83).

Asym-ψ-cumidine.

$$(CH_3{:}CH_3{:}CH{:}_3NH_2{=}1{:}2{:}4{:}6)$$

is prepared by reduction of the corresponding nitro-compound with iron and acetic acid (Edler, Ber. 1885, **18**, 630), or with iron and sulphuric acid (Huender, Rec. trav. chim. 1915, **34**, 11), m.p. 36°, b.p. 233°, soluble in water.

CUMIN or CUMMIN. The dried fruit (seed) of *Cuminum Cyminum* Linn. (Fam. Umbelliferæ), a small annual plant indigenous to Egypt, but cultivated in other parts of Northern Africa, Southern Europe and India. The fruits are about 4 to 6 mm. long, tapering towards both base and apex, resembling caraways and, in fact, they have been called Roman caraways. The mericarps are less curved than those of caraway, and whilst they are usually separate, they may be attached to the pedicel. Each mericarp has five longitudinal ridges densely covered with numerous hairs, alternated with secondary ridges. The cross-section of the fruit reveals four dorsal vittæ, or essential oil ducts, and an oily endosperm. The flavour and odour are reminiscent of both caraway and anise, but are more bitter and less agreeable. It is used as a constituent of curry powder and as a carminative, the latter chiefly in veterinary practice.

Microscopic Appearance.—The hairs are seen to be part of the pericarp, measuring up to 200μ in length and from 25 to 40μ in breadth, and are composed of elongated cells. These are distinctive of the fruit. The vittæ on the outer surfaces measure up to 200μ in diameter, whilst those of the commissural side are even larger. Each of the primary ribs contains a bundle of fibres about 50μ in diameter. The endosperm contains fixed oil and aleurone grains which are 15μ or less in diameter and enclose rosettes of calcium oxalate.

Chemical Composition.—C. Arragon (Ann. Falsif. 1915, **8**, 345) quotes the following composition of a sample of cumin fruit from Holland:

	%
Water	10·5
Ash	7·27
Fat	22·9
Essential oil	2·3
Protein	22·6
Fibre	13·4
Reducing substances, starch, etc.	20·4

All figures, except water, are on the dry material.

The principal constituent is the essential oil, and probably the most satisfactory method of determining this is by the process of Cocking and Middleton (Quart. Pharm. 1935, **8**, 435). The powdered fruit is mixed with brine and distilled, the vapours being passed through the top of a condenser into a graduated tube, in which the oil is collected whilst the condensed water is returned to the distillation flask. An air inlet and outlet are provided by a side tube below the condenser, but above the graduated tube. Cumin contains from 2·5 to 4·0% of essential oil (*q.v.*).

Standards.—The "British Pharmaceutical Codex" suggests that not more than 2% of foreign organic matter should be present.

T. McL.

CUMIN, ESSENTIAL OIL OF. The oil distilled from the fruits of *Cuminum Cyminum* Linn. (Fam. Umbelliferæ), a native of Egypt and the Mediterranean, and cultivated in India and China. The chief supplies are from Morocco, Malta, and Sicily; yield 2·5 to 4·0%.

Composition.—The chief constituent is cumic or cuminic aldehyde, of which 30 to 40% is present. Pinene, cymene, dipentene, β-phellandrene are present.

Characters.—A colourless or pale yellow oil darkening on keeping. Sp.gr. 0·900–0·935, opt. rotation +3° to +8°, ref. ind. 1·495–1·509. Soluble in 10 volumes 80% alcohol. The cumic aldehyde is determined by the hydroxylamine process (*v.* ALDEHYDES).

C. T. B.

CUMMIN *v.* CUMIN.

CUPFERRON. Ammonium-nitroso-β-phenylhydroxylamine. Used as a reagent for **Cu**, and also in the separation of **Fe**, **Ti**, and **Zr** *v.* Chemical Analysis, Vol. II, p. 583.

CUPRASE. Colloidal cupric hydroxide.

β-*iso*CUPREIDINE (*isoapo*QUINIDINE) *v.* Cinchona Alkaloids (this vol., p. 170*d*).

CUPREINE *v.* Cinchona Alkaloids (this vol., p. 160*d*).

CUPRENE *v.* Acetylene.

CUPRETENINE *v.* Cinchona Alkaloids (this vol., p. 178*b*).

CUPRI-ADEPTOL. Copper *m*-phenol sulphonate.

CUPRITE. Native cuprous oxide, Cu_2O, crystallising in the cubic system. Brilliant, transparent crystals of a ruby-red colour (hence the name ruby-copper-ore) are not uncommon; sp.gr. 6·0. In the variety called *chalcotrichite*, the crystals are capillary in form, being enormously elongated in the direction of one of the cubic edges, and are loosely matted together in plush-like masses. Another variety, known as *tile-ore* (Ger. *Ziegelerz*), is earthy or compact and of a brick-red or brownish colour; it consists of an intimate mixture of cuprite and limonite, and has resulted from the alteration of chalcopyrite. Cuprite is sometimes of importance as an ore in the upper oxidised portions of copper veins.

L. J. S.

CUPROL. Copper salt of nucleinic acid. External astringent dressing (*Parke Davis, London*). B.P.C. 1934.

CUPRON, α-benzoin oxime, used in the quantitative determination of copper and molybdenum *v.* Chemical Analysis, Vol. II, p. 605*d*.

CUPROSILICON. *Cuprous silicide* (*v.* Copper).

CUPRUM LAZUREUM *v.* Azurite.

CURACIT-SODA. A mixture of the sodium salts of glycocholic and other acids obtained from ox gall, used as a wetting-out agent.

CURARE. Other native names, *Curara, Urari, Woorari, Woorali, Woorara.* Curare is the name given to the arrow poisons of S. American Indians who dwell in the region of the Orinoco and Amazon rivers. Knowledge of it was first brought to Europe by Sir Walter Raleigh in 1595, and from that time to the present its origin and preparation have been discussed by explorers, botanists and chemists. A summary of the earlier observations of La Condamine, Humboldt and Bonpland, Waterton, Schomburgk, Castelnau, Thirion, Jobert and Crévaux is given by Planchon (Pharm. J. 1880, [iii], **11**, 469, 491, 529, 589, 693, 754). It is now known that curare is an aqueous decoction of several plants, one of which is usually a species of *Strychnos*, to which the toxic action of the preparation is due. The remainder contribute extractives which give the curare the consistency necessary for preservation of the poison and for tipping the arrows. The plants used in the preparation of the product vary with the locality as the following shows:

Sources of Curare.—(1) Upper Amazon: *Strychnos Castelnaeana*, Baill., *S. Yapurensis*, Planch.

(2) Upper Orinoco: *S. Gubleri*, Planch.

(3) British Guiana: *S. toxifera*, Schomb.; *S. Schomburgkiana*, Klotzsch.; *S. cogens*, Benth.

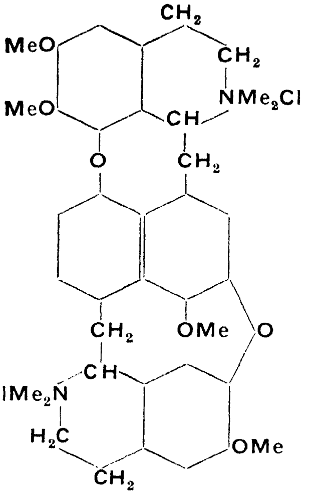
(4) Upper French Guiana: *S. Crevauxii*, Planch.

(5) Esmeralda (Venezuela): *S. guianensis*, Aubl.

(6) Peruvian Amazon: *Chondrodendron* spp. (?).

The advent of firearms replaced arrows for hunting, and curare rarely appears nowadays on the European market. Such curare as is found in museums, pharmaceutical houses, and physiological laboratories consists of a brown to black, often brittle, extract with a bitter taste. In medicine it has been used in the treatment of tetanus, hydrophobia, epilepsy, and in cases of chronic nervous disease with predominant muscular rigidity. For a summary, *see* West (Proc. Roy. Soc. Med. 1935, **28**, 41). As native preparations vary considerably in composition the greatest care is necessary in the administration of the drug and its efficacy must first be tested on animals.

For the earlier chemical investigations on curare, *see* Flückiger (Arch. Pharm. 1890, **228**, 78). The foundation of our chemical knowledge was laid by Boehm (Chem. Zentr. 1895, **2**, 1084; 1897, **2**, 1078; Arch. Pharm. 1897, **235**, 660) who examined the three kinds of curare, distinguished by their containers, which have at various times appeared in some quantity on the European market. Boehm showed that the highly active principle in each case was a different quaternary alkaloid. *Tubocurare* or *para curare* was imported in bamboo tubes and contained a crystalline inactive tertiary alkaloid *curine* which was shown later by Späth, Leithe, and Ladeck (Ber. 1928, **61**, [B], 1698) to be the *lævo*-enantiomorph of *d*-bebeerine, an alkaloid found in *Radix Pareiræ bravæ* (*Chondrodendron tomentosum*, R. and P.). Its formula is $C_{36}H_{38}O_6N_2$ (Späth and Kuffner, Ber. 1934, **67**, [B], 55) and the structure of its di-**O**-methyl ether is now known in detail. It belongs to the group of bisbenzyl*iso*quinoline alkaloids which are formed by fusion of two benzyl*iso*quinoline structures through ether linkages (Faltis, Kadiera, and Doblhammer, Ber. 1936, **69**, [B], 1269; King, J.C.S. 1936, 1276). The amorphous quaternary alkaloid called *tubocurarine* by Boehm, was crystallised by King (J.C.S. 1935, 1381) and found to produce complete "curare" paralysis of the frog on a dose of 0·5 mg. per kg. within 15 minutes. It was also shown (King, *l.c.*) that *d*-tubocurarine chloride had the properties of a phenolic betaine and on complete methylation of the phenolic groups gave *d*-**O**-methyltubocurarine chloride which proved to be a diastereoisomeride of *d*-**O**-methylbebeerine methochloride (I). It is very probable that tubocurare is prepared from some species of *Chondrodendron* hitherto not examined chemically and growing in the region of the Peruvian Amazon.



O-Methyltubocurarine chloride.
O-Methylbebeerine methochloride.
I.

Calabash or *gourd curare* was found by Boehm to contain an amorphous quaternary alkaloid, $C_{19}H_{25}ON_2Cl$, called *curarine*, together with traces of a non-quaternary alkaloid. The same amorphous quaternary alkaloid was isolated from *Strychnos toxifera* Schomb. (King, Nature, 1935, **135**, 469) thus confirming Robert Schomburgk's discovery of *S. toxifera* as the main sources of the active ingredient of the curare of the Macus Indians from British Guiana. It paralysed frogs on a dose of 0·125 mg. per kg. and showed colour reactions reminiscent of strychnine.

The third variety, known as *pot curare*, comes from Brazil, and appeared on the market in small jars usually of unglazed clay. Boehm found that this curare varied widely in activity but from active material was able to isolate two relatively inactive non-quaternary alkaloids, *protocurine*, $C_{20}H_{23}O_3N$, needles, m.p. 306° (decomp.), and *protocuridine*, prisms, m.p. 274–276°, and an active amorphous quaternary base *protocurarine* of uncertain composition. The last-mentioned showed colour reactions similar to strychnine. The paralysing dose on frogs was 0·13 mg. per kg. (Jacabhazy, Arch. exp. Path. Pharm. 1899, **42**, 10). It is probable that the active principle is contributed by *Strychnos Castelnaeana* Wedd., and not improbable that other species, such as *Cocculus toxicoferus*, Wedd. and *Anomospermum grandifolium* Eichler supply some of the alkaloids present.

The predominant pharmacological action of curare consists in a paralysis of the nerve endings of voluntary muscle, and for this reason it is much used in physiological research. The discovery by Boehm that the "curare" principle in the three best known types of curare is a quaternary alkaloid is noteworthy since it is a pharmacological commonplace that nearly all ammonium bases paralyse motor nerve endings of voluntary muscle (Crum-Brown and Fraser, Proc. Roy. Soc. Edin. 1869, **6**, 560).

The recent investigations of Freise in S. America (Pharm. Ztg. 1933, **78**, 852; 1936, **81**, 818) show that a pot curare of the Chavante Indians of Southern Brazil is employed for killing animals to be used as food and is exported as an article of trade to the Argentine. It contains as its active principle a non-quaternary alkaloid, *macoubeine*,

$$C_{22}H_{26}O_2N_2{\cdot}4H_2O,$$

$[\alpha]_D$ −55·5°, which is devoid of the typical "curare" action of the pharmacologist. For this reason it is better described as a "false curare." It is prepared from *Macoubea Guyanensis* Aubl. (Fam. Apocynaceæ).

H. K.

CURARINE *v.* CURARE.

CURCAS OIL (purging nut oil, physic nut oil, *Oleum infernale*; Fr. *huile de pulghère*, — *de purghère*, — *de gros pignon d'Inde*), is obtained from the seeds of *Jatropha curcas* L. (Fam. Euphorbiaceæ), a shrub or small tree, probably indigenous to Central America, but growing freely or under cultivation in many parts of the tropics, and especially in the Portuguese colonies. In the Cape Verde Islands, where the cultivation of curcas is second only to that of coffee, the export of seed to Lisbon amounted to as much as 3,000 tons in 1930 and about 2,000 tons in succeeding years (*cf.* J. Cunha da Silveira, Anais do Instituto superior de agronomia (Lisbon), 1934, **6**, fasc. 1, 116); in Réunion the plant is grown as a support for the vanilla plant. The seeds consist of from 32–40% of husk and 60–68% of kernel, containing from 46–58% of oil (*i.e.* about 30–40% on the whole seed) which is recovered commercially by hot expression. The oil is pale in colour, becoming reddish-yellow upon exposure to the air, and has a viscosity about equal to, or slightly greater than, that of olive oil: it is characterised by a disagreeable odour, and possesses emetic and strongly purgative properties, which are much more pronounced than those of castor oil [1]: it is distinguished from the latter by its lack of optical activity, low acetyl value and viscosity, and by its sparing solubility in alcohol and ready miscibility with light petroleum. It differs from croton oil (*q.v.*) in possessing no rubefacient or vesicant properties.

The recorded analytical values for curcas oil show considerable variations (probably depending partly upon the origin of the seed), but the following ranges are typical for genuine expressed oils: f. pt. *c.* −13°C., sp.gr.$^{15}_{15}$ 0·918–0·921, acid value 0·7 to 9·2, saponification value 190–193, iodine value 93–100, acetyl value 5–10 (figures of 18 and 25 were recorded for two samples examined at the Imperial Institute (Bull. Imp. Inst. 1921, **19**, 288). Samples of oil extracted by petroleum spirit from decorticated seeds and examined by Droit (Thesis, Paris, 1932; François and Droit, Bull. Soc. chim. 1933, (iv), **53**, 728; African seeds extracted in the cold), and by Adriaens (IV^{e} Congr. Intern. Tech. Chim.

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[1] A mixture of castor oil and curcas oil, sold under the name of "English castor oil" is stated to have been a popular purgative in America and the Antilles in the last century (*see* Düss, Ann. Inst. Col. Marseilles, 1896, **3**, 26).

Ind. Agric., Bruxelles, 1935; Bull. Mat. Grasses, 1936, **10**, 813; seeds from Belgian Congo), had sp.gr.$^{15}_{15}$ 0·9122–0·9219, ref. ind.^{15} 1·4694–1·4730, acid value 0·4–7·8, saponification value 176–180 (Droit), 193–196 (Adriaens); iodine value 97–98 (Droit), 96·6–106·9 (Adriaens); acetyl value 4·5–8·5, unsaponifiable matter 0·1–1·15%, including a phytosterol and a resinous material (Droit).

Whilst the commercial oils do not crystallise on exposure to low temperatures, the oils extracted in the laboratory gradually deposit crystals which appear to consist chiefly of oleodistearin. According to the detailed examination by Droit, the fatty acids of curcas oil consist solely of stearic, palmitic, myristic, oleic and linolic acids; no trace of ricinoleic or other hydroxy-acid (such as the "curcinoleic acid," the presence of which was reported by Siegel and other early investigators) could be found (*cf.* Klein, Z. angew. Chem. 1898, **11**, 1012). The "isocetic" acid isolated by Bouis (Compt. rend. 1854, **39**, 923) appears to have been a mixture of palmitic and myristic acids. The medicinal use of the oil is limited by the presence in it of a toxic principle (a sterol-resin ester?) which is associated with the alcohol-soluble fraction of the oil (*cf.* Cadet de Gassicourt, J. de Pharm. (Paris), 1824, **10**, 170; Soubeiran, *ibid.* 1829, **15**, 500; Felke, *l.c.*, *infra*; Droit, *l.c.*, *infra*), and is not destroyed by heating for 1½ hours at 100°C.; upon saponification, this fraction yields fatty acids, a phytosterol, and a resin, none of which appears to have any physiological action when examined separately (Droit, Bull. Mat. Grasses, 1932, **16**, 270).

A second poisonous substance, *curcine* (a toxalbumin) (*cf.* Stillmark, Arb. Pharm. Inst. Dorpat, 1889, **3**, 149; Siegel, Thesis, Dorpat, 1893; Felke, Landw. Versuchs-Stat. 1913, **82**, 427) is found in the decorticated seeds after removal of the oil, and, consequently, the by-product seed-cake can only be utilised as a fertiliser. Curcas seeds further contain a fairly active lipase (Grimme, Z. deut. Öl-Fett-Ind., 1921, **41**, 513).

In addition to its use in medicine, curcas oil is used in the manufacture of soap (both in the tropics and in Europe), and to a limited extent as a burning oil; its use as a substitute for olive oil in compound lubricating oils has been suggested. The oil thickens somewhat on heating, and is frequently reported to possess weak drying properties (*cf.* Bull. Imp. Inst. 1921, **19**, 288); this propensity appears to be less well marked, however, in the oils from the Congo (Adriaens, *l.c.*).

(For a detailed study of the purging nut, its oil and toxicology, and bibliography, *see* Droit, *l.c.*; also Anon., Gov. Lab. Bangkok, 1929, No. 4, 8).

E. L.

CURCINE *v.* CURCAS OIL.

CURCUMENES, THE. The essential oil from the rhizomes of *Curcuma aromatica* contains a mixture of two monocyclic sesquiterpene hydrocarbons $C_{15}H_{24}$, *α*- and *β-curcumenes* (Rao, Shintre and Simonsen, J. Indian Inst. Sci. 1926, **9**, A, 140; Rao and Simonsen, J.C.S. 1928, 2496). *l*-*α*-Curcumene, purified through its *monohydrochloride*, b.p. 150–155°/8 mm., has b.p. 128–130°/7 mm., d^{30}_{30} 0·8633, n^{30}_{D} 1·4944, $[\alpha]_D$ −22·9°. It contains three ethylenic linkages and is best characterised by the preparation of its *nitrosate*, m.p. 101°. *l*-*β*-Curcumene, which can be purified through its *trihydrochloride*, m.p. 84–85°, has b.p. 128–130°/6 mm., d^{30}_{0} 0·8810, n^{30}_{D} 1·4949, $[\alpha]_D$ −27·9°. It has three ethylenic linkages. The constitutions of these hydrocarbons have not been determined.

J. L. S.

CURCUMIN (*Turmeric yellow*), the yellow substantive dye and indicator from the roots of *Curcuma* species Linn.

CURINE *v.* CURARE.

CURITE, $2PbO{\cdot}5UO_3{\cdot}4H_2O$, a uranium mineral.

CURRANT. The fruit of bushy species of *Ribes*. Two varieties are commonly met, the red currant, *R. rubrum* (or *R. vulgare* Lam.), and the black currant, *R. nigrum*, L. Variants of *R. rubrum* in which the fruit is white are specially favoured for dessert.

Analyses of the red currants from American and European sources respectively are:

	Total solids.	Protein.	Acids (as citric).	Invert sugar.	Sucrose.	Pectin.	Ash.
	%	%	%	%	%	%	%
(1)	12·97	1·37	2·21	3·44	0·0	0·8	0·6
(2)	15·29		1·90	5·74	0·46		0·57

(1) Munson *et al.*, U.S. Dept. Agric. Bur. Chem. Bull. 1905, No. 66.
(2) Olig, Z. Unters. Nahr.-Genussm. 1910, **19**, 558.

According to Hotter (Z. landw. Versuchsw. 1906, **9**, 747) the proportion of fructose is slightly higher than that of glucose. The actual amounts of sucrose present in the fruit and the proportion of reducing to non-reducing sugars varies considerably with the stage of ripeness of the currant. Sobolevskaja and Turetzkaja (Bull. Acad. Sci. U.R.S.S. [Classe sci. math.], 1934, **9**, 1341), have observed the steady increase in total sugars and in the ratio of invert sugar to sucrose as the fruit develops. The absolute amount of sucrose, however, increases markedly during the final stages of ripening. These authors explain the general course of sugar changes in the ripening fruit thus:

$$\text{sucrose} \rightarrow \text{glucose} + \text{fructose} \rightarrow \text{polysaccharide} \rightarrow \text{glucose} + \text{fructose}.$$

The accumulation of sucrose in ripened fruit is ascribed to the cessation of its decomposition rather than to its re synthesis from invert sugar; the simultaneous increase in invert sugar is attributed to the hydrolysis of polysaccharides. The acidity of the fruit is due almost entirely to citric acid, although small amounts of malic acid are occasionally reported.

The seeds of red currants contain water 11·42, protein 14·92, fat 23·6, **N**-free extract 24·4, fibre 22·8, and ash 2·78 (Alpers, Z. Unters. Nahr.-Genussm. 1916, **32**, 499). The characteristics of the expressed oil are d_{15} 0·9288, ref. ind. 1·4772 (25°), saponification value 194·5, iodine value 159·8, Reichert-Meissl value 0·55, Polenske value 0·5, Hehner number 95·6, acid value 12·9, unsaponifiable matter 0·64%.

The mineral constituents of red currants (in terms of fresh fruit) include: total ash 0·41, K_2O 0·19, Na_2O 0·02, CaO 0·08, MgO 0·03, P_2O_5 0·09, Fe 0·0007, Al 0·0015, Zn 0·0002%.

Windisch and Schmidt (Z. Unters. Nahr.-Genussm. 1909, **17**, 584) record the following as average analyses of the juice of red currants: d_{15} 1·045, solids 11·65, protein 0·34, acids (as citric) 2·11, invert sugar 6·90, total ash 0·48 g. per 100 c.c.

The black currant resembles the red species in composition in many respects. Detailed analyses are, however, less common. Hotter (*l.c.*) records the following analysis for black currant pulp: solids 20·7–20·9, acids (as malic) 2·3–3·4, total sugars 7·3–7·9, glucose 3·3–3·5, fructose 4·0–4·4, sucrose 0·2–0·4, tannin 0·33–0·41, ash 0·63–0·87.

The acids of the fruit comprise chiefly citric and tartaric; the proportions vary with stage of ripening, that of citric acid reaching maximum in the half-ripe stage.

As in the case of red currants the black variety undergo a very rapid increase in sugar content in the last stages of ripening (or over-ripening).

A. G. Po.

CURTIUS DEGRADATION OF ACID AZIDES *v.* Amines.

CUSCAMIDINE *v.* Cinchona Alkaloids (this vol., p. 161*c*).

CUSCAMINE *v.* Cinchona Alkaloids (this vol., p. 161*c*).

CUSCOHYGRINE *v.* Cocaine and other alkaloids of the Erylhroxylon species.

CUSCONIDINE *v.* Cinchona Alkaloids (this vol., p. 161*d*).

CUSCONINE *v.* Cinchona Alkaloids (this vol., p. 161*d*).

CUSPARIA BARK, CUSPARINE, GALIPINE AND MINOR ALKALOIDS. Cusparia bark, Angostura bark, *Cortex Cuspariæ*; (Fr. *Écorce d'Angosture*; Ger. *Angosturarinde*). It is derived from *Galipea officinalis* Hancock, syn. *Cusparia trifoliata* Engler (Fam. Rutaceæ), a small tree of Venezuela, and was originally shipped from Angostura on the Orinoco to Trinidad. It was long considered to be derived from the closely related *Cusparia febrifuga* D.C. Brazilian (false) "Angostura" bark is derived from *Esenbeckia febrifuga* A. Juss. (Fam. Rutaceæ). For history and botanical investigation of different barks *v.* Hartwich and Gamper (Arch. Pharm. 1900, **238**, 568).

Angostura bark contains about ten alkaloids, some of which are very simple basic compounds; it also contains a little essential oil, a bitter principle and a glucoside.

The cusparia alkaloids were investigated by Tröger and Beckurts; for references concerning earlier investigations, *v.* Späth and Brunner (Ber. 1924, **57**, [B], 1243).

The best description for *isolation* and identification of cusparia alkaloids is given by Späth and Eberstaller (Ber. 1924, **57**, [B], 1687), Späth and Papaioanou (Monatsh. 1929, **52**, 129), and Späth and Pikl (Ber. 1929, **62**, [B], 2244; Monatsh. 1930, **55**, 352). 16 kg. of angostura bark are percolated with EtOH for 8 days. EtOH is evaporated *in vacuo* and the oily residue still containing appreciable amounts of EtOH (this is essential) diluted with 2 litres of 20% NaOH and extracted with 4 litres of Et_2O. Phenolic and non-phenolic bases are thus separated.

Non-phenolic Bases.—By extracting above ethereal solution with 1% HCl the sparingly soluble hydrochlorides of *cusparine* (I) and *galipine* (II) are obtained. The two alkaloids are separated through the oxalates, a method developed by Tröger and Kroseberg (Arch. Pharm. 1912, **250**, 503; (I)-oxalate sparingly, (II)-oxalate easily, soluble in H_2O). Yields: (I) 1·06%, (II) 0·35%.

200 g. of the oily mixture left after separation of (I) and (II) are treated with light petroleum, which dissolves about 30 g. The oily residue obtained by evaporation of the petroleum is steam-distilled and the distillate re-distilled *in vacuo*, after a small first fraction A, 8·7 g. of almost pure 2-n-*amyl*-4-*methoxy-quinoline* (III) distils at 190–200°/14 mm.; yield 0·05%.

The first fraction A is distilled again, when two separate fractions are obtained: b.p. 100–145°/14 mm.—B (0·5 g.) and b.p. 145–190°/14 mm.—C (5·2 g.). Fraction B finally yields *quinoline* (IV) and 2-*methylquinoline* (quinaldine) (V). Yield of the two bases about 0·003%. Fraction C gives 1-*methyl*-2-*keto*-1-2-*dihydroquinoline* (VI) (0·01%) and 2-n-*amylquinoline* (VII) (0·003%).

Phenolic Bases.—The alkaline solution left after separation of the non-phenolic bases is acidified with 5% HCl, separated from tar, basified with soda, and extracted with $CHCl_3$. After evaporation the residue is extracted with ether and finally pure *galipoline* (VIII) is obtained.

Cuspareine (Chem. Zentr. 1909, II, 1570; 1911, I, 163), *galipoidine* (Arch. Pharm. 1913, **251**, 252), and *angosturine* (Chem. Zentr. 1911, I, 163) were isolated by Tröger and co-workers, but their existence has not yet been confirmed. All cusparia alkaloids are optically inactive.

Cusparine (I), $C_{19}H_{17}O_3N$, crystallises in needles from light petroleum, m.p. 92°, it is apparently trimorphous (colourless needles, yellow needles, and amber-tinted crystals). (I) is easily soluble in organic solvents. The salts are sparingly soluble and may be readily separated from the salts of associated alkaloids. $B{\cdot}HCl+3H_2O$, white crystals; B·oxalate is characteristic (*v. supra*), m.p. 152–156°, sulphur-yellow needles. Also platinichloride and aurichloride are crystalline. B·methiodide, m.p. 176° (yellow prisms). (I) is the easiest of the angostura alkaloids to separate.

Galipine (II), $C_{20}H_{21}O_3N$, crystallises from EtOH, Et_2O or light petroleum in colourless prisms, m.p. 115·5°; it yields crystalline salts, which are more soluble than those of (I). B·HBr, m.p. 169° (yellow); B·HI, m.p. 178° (yellow); B·methiodide, m.p. 145° (yellow needles).

2-n-*Amyl*-4-*methoxy-quinoline*(III), $C_{15}H_{19}ON$, colourless oil with very faint odour, easily soluble in dilute HCl, B·picrate, needles from MeOH, m.p. 132°; $B_2{\cdot}$platinichloride forms characteristic, yellow crystals, m.p. 220° (decomp.).

Quinoline (IV) and 2-*methylquinoline* (V) (quinaldine) were identified as picrates and 2:4:6-trinitro-1:3-cresolates.

1-*Methyl*-2-*keto*-1:2-*dihydroquinoline* (VI), $C_{10}H_9ON$, m.p. 74°; **B**·picrate from **MeOH**, m.p. 129–130°.

2-n-*Amylquinoline* (VII), b.p. 130–145°/10 mm., identified as picrate, m.p. 125–126° (from **MeOH**).

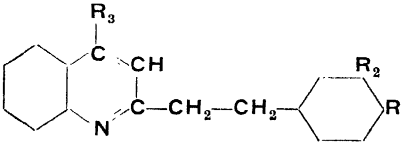
Galipoline (VIII), $C_{19}H_{19}O_3N$, colourless crystals, m.p. 193° (from H_2O), soluble in caustic soda; by methylation of (VIII) with diazomethane (II) is obtained.

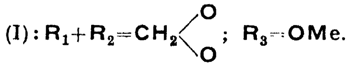
Cuspareine (*cf.* Tröger and Runne, Arch. Pharm. 1911, **249**, 176), $C_{18}H_{19}O_2N$, m.p. 56°, is a very weak base and distils without decomposition. No salts could be obtained, it contains two **MeO**-groups. **B**·methiodide, m.p. 156° (leaflets from H_2O).

Galipoidine (*cf.* Tröger and Runne, *l.c.*, 183), $C_{19}H_{15}O_4N$, m.p. 233°, needles from **EtOH**, insoluble in ligroin, light petroleum and benzene; sparingly soluble in hot **EtOH**. It yields a crystalline platinichloride and aur chloride.

Angosturine is apparently identical with galipoidine (*cf.* Chem. Zentr. 1911, I, 164).

Constitution of Angostura (Cusparia) Alkaloids.—When (I)-methiodide is treated with silver oxide or caustic soda, a new base, *iso*cusparine (m.p. 194°), is formed. (II)-methiodide undergoes the same rearrangement. Apparenty the **Me** of the **MeO**-group migrates to the **N**-atom (*cf.* Tröger and Müller, Arch. Pharm. 1914, **252**, 459), a rearrangement which is typical for α- and γ-methoxy-quinolines (*cf.* dictamnine and skimmianine). By zinc dust distillation of cuspareine (Tröger and Runne, *l.c.*, 182) and (II) (Tröger and Kroseberg, *l.c.*, 525) quinoline was obtained. By potash-fusion both (I) and (II) yielded protocatechuic acid, on oxidation with permanganate veratric and a methoxyquinoline carboxylic acid were obtained from (II). Tröger and Bönicke (Arch. Pharm. 1920, **258**, 250) suggested a formula for (II) which was slightly modified by Späth and Brunner (*l.c.*); (I), (II), and (VIII) have the following formulæ, as proved by synthesis:




$(I): R_1+R_2=CH_2\langle{}^{O}_{O}\rangle$; $R_3=OMe$.

$(II): R_1=R_2=R_3=OMe$.
$(VIII): R_1=R_2=OMe;\ R_3=OH$.

Synthesis of (I): Späth and Brunner (*l.c.*).
Synthesis of (II): Späth and Eberstaller (*l.c.*).
Synthesis of (III): Späth and Pikl (*l.c.*).
Synthesis of (VIII): Späth and Papaioanou (*l.c.*).

Nothing is known about the constitution of cuspareine and galipoidine.

The essential oil (from *Cusparia trifoliata*) is described in Schimmel and Co.'s Semi-Annual Report, April, 1913.

Angosturin, $C_9H_{12}O_5$, m.p. 58°, is a crystalline bitter principle, readily soluble in H_2O and **EtOH**, but not in $(Et)_2O$. Angostura bark is a constituent of "Angostura bitters," and is used in medicine as a tonic in derangements of the alimentary canal, but it is not included in the "British Pharmacopœia" nor in the "United States Pharmacopœia."

Schl.

CUSPARINE *v.* Cusparia Bark.

CUSSO, KOUSSO. The dried panicles of pistillate flowers of *Brayera anthelmintica* Kunth.

CUTCH *v.* Catechu.

CYAMELIDE *v.* Cyanides (this vol., p. 505).

CYANAMIDE *v.* Cyanides (this vol., p. 505).

CYANANTHROL B (SOLWAY BLUE R) *v.* Anthraquinone Dyestuffs.

CYANIC ACID *v.* Cyanides (this vol., p. 506*d*).

CYANIDATION PROCESS FOR GOLD AND SILVER ORES *v.* Cyanides.

CYANIDES.

Historical.—The earliest known cyanide compound was Prussian blue, which was discovered accidentally in 1704 by Diesbach and Dippel in an attempted preparation of Florentine lake. The new blue very quickly displaced ultramarine, but its method of manufacture remained a secret until 1724, when Woodward described the calcination of blood with potassium carbonate, and the treatment of the aqueous extract with ferrous sulphate and alum to give a greenish precipitate, which yielded Prussian blue when treated with hydrochloric acid. Macquer showed that horn, leather and other animal matter could be used instead of blood, and in 1752 found that Prussian blue was decomposed by boiling with alkali into ferric hydroxide and a soluble salt from which the blue could be regenerated. Potassium ferrocyanide (yellow prussiate) was first obtained in the crystalline form by Sage in 1772.

The relationships of the ferrocyanides, hydrocyanic acid, cyanogen and many of their derivatives were elucidated by the brilliant researches of Scheele (1782–3), Berthollet (1790), and Gay Lussac (1815). Scheele was the first to prepare an aqueous solution of hydrocyanic acid and Gay Lussac first isolated the anhydrous liquid.

Animal matter treated by the process described above was the sole source of cyanides for about 150 years, until a new one was found in the cyanogen content of coal gas. The existence of cyanogen compounds in coal gas was mentioned by Jacquemyns in 1843, and in 1860 prussiate was manufactured from spent oxide for the first time at the Paris gas works. By 1884 gas works ferrocyanide had almost completely replaced the older product in the European industry, partly because of the increased use of nitrogenous organic matter as a fertiliser, and partly because of the reduced consumption of Prussian blue due to the competition of coal tar dyes. In the United States the old process held its own for nearly twenty years longer. Between 1890 and 1900, greater efficiency in the recovery of cyanides from coal distillation products was obtained by the introduction at gas works of special cyanide washers, the cyanide being almost quantitatively fixed as ferrocyanide which is relatively easily recovered from the scrubbing liquid.

The discovery of the electroplating process for gold and silver by J. R. and H. Elkington in 1840 led to a demand for potassium cyanide, which was met by the process of fusing ferrocyanide with potassium carbonate, a reaction discovered in 1834 by F. and E. Rodgers. In 1887 MacArthur and the Forrests patented the cyanide process for the extraction of gold and silver from their ores, and it was first operated at Karangahake, New Zealand, in 1889, and near Johannesburg, Transvaal, in 1890. The cyanide process was rapidly adopted in all the goldfields of the world, and led to a considerable increase in the rate of gold production, and transformed the cyanide industry from a small by-product industry into a relatively large synthetic industry. Whilst the production of potassium cyanide in 1889 (by the Rodgers process) was 50–70 tons per annum, and of yellow prussiate not more than 5,000 tons, it is estimated that the world production of potassium cyanide had reached 6,500 tons per annum by 1899.

At first the increased quantities of cyanide were made from ferrocyanide by the Rodgers process, and then by the Erlenmeyer process (discovered in 1876) using metallic sodium. The rapidly increasing demand, however, stimulated the search for direct synthetic processes, of which a great number were invented and the following were actually worked with some success:

Process.	Location of plant.	Date of first production.
Siepermann	Stassfurt, Germany	1892
Beilby	Glasgow, Scotland	1892
British Cyanides Co.	Oldbury, England	1895
Raschen	Runcorn, England	1898
Readman	Leven, Scotland	1899
Castner	Germany, Scotland, U.S.A.	1899 1900
Bueb (Schlempe)	Dessau, Germany	1902

Of these the last two are still in operation and provide the greater part of the world's cyanide requirements. At the present time there is a tendency in the United States for a reversal of the old economic relationship, so that synthetic cyanide is the raw material for ferrocyanide.

The use of cyanide as a fumigant in pest control was introduced in 1903, first in the citrus groves of California to control a parasitic scale insect, and at a later date in the fumigation of ships and warehouses and other buildings against vermin. The hydrocyanic acid vapour required was formerly generated *in situ* from cyanide and acid, but since 1917 liquid hydrocyanic acid has been marketed for direct application.

Another use of cyanide which has been developed since 1918 is in the case-hardening of iron and steel, which now consumes increasing quantities of sodium cyanide. This use depends on the formation of a surface layer of a solid solution of iron carbide and iron nitride in metallic iron.

The source of the nitrogen for the commercially successful cyanide processes is ammonia or methylamines (Schlempe process), but the War (1914–18) stimulated the search for methods of fixing atmospheric nitrogen as cyanide. Possoz and Boissière first attempted the manufacture of potassium cyanide from potassium carbonate, charcoal, and nitrogen as early as 1843, but the greatest advance towards the technical realisation of this reaction was made by Bucher in the United States between 1912 and 1918. With the stimulus of abnormal war conditions removed, however, the process was unable to compete with the older methods, and its operation is now discontinued in America. About the same time Caro and Frank in Germany were endeavouring to produce cyanide by the nitrogenation of calcium carbide, and the process was brought to commercial success by Landis in America in 1918. Relatively large quantities of impure calcium cyanide, used in the gold-mining industry and in fumigation, are now produced by this reaction. That no greater development of the fixation of nitrogen as cyanide has occurred may be ascribed to the great progress which was made, both during and immediately after the War, in the manufacture of synthetic ammonia, which has now largely replaced by-product ammonia as the raw material for cyanide manufacture.

The most recent research on cyanide synthesis has been in the realm of high-temperature gas reactions for the production of hydrocyanic acid from ammonia (or nitrogen) and hydrocarbons, and on methods of converting the hydrocyanic acid so obtained into sodium cyanide of similar purity to the high-grade product of the Castner process. Of the many such processes described, only one, involving the passage of a gaseous mixture of nitrogen and hydrocarbon gas or vapour through an arc, is known with certainty to have been operated on a commercial scale. It may well be, however, that the future development of the cyanide industry will be along these lines.

The world consumption of cyanide at the present time is probably more than 30,000 tons per year of sodium cyanide or its equivalent. The abandonment of the Gold Standard in many countries since 1931 has caused an increased consumption by stimulating the gold-mining and base metal industries, and steady development has occurred in the use of cyanide for case hardening and fumigation.

The cyanide compounds are considered below under the following headings:

I. Complex iron cyanides (ferrocyanides, ferricyanides, pentacyanides).
II. Alkali metal cyanides.
III. Heavy metal cyanides (of copper, gold, mercury, silver, zinc).
IV. Alkaline earth cyanides.
V. Hydrocyanic acid.
VI. Cyanogen and its derivatives.
VII. Cyanates.
VIII. Thiocyanates.

I. COMPLEX IRON CYANIDES.

General Chemistry.—In this section a brief account is given of the chemical characteristics and relationships of the ferrocyanides and ferricyanides.

In all probability the simple parent substances, ferrous cyanide, $Fe(CN)_2$, and ferric cyanide, $Fe(CN)_3$, do not exist. Substances having the empirical composition of the expected ferrous cyanide are indeed produced in the dry way by heating ammonium ferrocyanide or hydroferrocyanic acid, and in the wet way by precipitating ferrous solutions with cyanide; but these are rather to be regarded as ferrous ferrocyanide, $Fe_2[Fe(CN)_6]$, and similar complex derivatives of hydroferrocyanic acid, which are "polymers" of $Fe(CN)_2$ (*see* Wyrouboff, Ann. Chim. Phys. 1869, [iv], **16**, 280; Hofmann, Arnoldi and Hiendlmaier, Annalen, 1907, **352**, 54). Analogous preparations of $Fe(CN)_3$ are lacking, for the thermal decomposition of ammonium ferricyanide and hydroferricyanic acid has not been studied, and only ferric hydroxide is produced by the interaction of cyanide with ferric salt solutions. A crystalline solid of the composition $Fe_2(CN)_6,2H_2O$ has been prepared by Reihlen and von Kummer (Annalen, 1929, **469**, 30) from solutions of potassium ferricyanide and ferric nitrate, and this is most probably ferric ferricyanide, $Fe[Fe(CN)_6]$.

The iron hexacyanide ions are among the most stable complexes encountered in inorganic chemistry, the degree of dissociation into simpler ions being too small to be measured. It appears unlikely that a dissociation yielding the simple ferrous or ferric ions occurs at all, and when Fe^{++} or Fe^{+++} and CN' are brought together, formation of complex iron cyanide ions proceeds until one or other of the constituent ions has disappeared. This explains the failure of attempts to prepare the simple ferrous and ferric cyanides by wet reactions. The formation of ferrocyanides from cyanides occurs with insoluble as well as soluble ferrous compounds, and even with metallic iron itself. The ionic equations

(*a*) $Fe^{++}+6CN'=Fe(CN)_6''''$
(*b*) $FeS+6CN'=Fe(CN)_6''''+S''$
(*c*) $Fe(OH)_2+6CN'=Fe(CN)_6''''+2OH'$
(*d*) $Fe+2H_2O+6CN'$
$=Fe(CN)_6''''+2OH'+H_2$

testify further to the extreme stability of the ferrocyanide ion, for if any appreciable dissociation into ferrous ions occurred, the solubility product of ferrous sulphide (*b*) or ferrous hydroxide (*c*) and (*d*) would be exceeded and the reaction reversed.

Ferricyanides cannot be synthesised from cyanides and ferric compounds by reactions analogous to those mentioned above, for cyanides can reduce ferric salts and ferric hydroxide, so that ferrocyanides result. According to Rupp (Z. anal. Chem. 1931, **86**, 217), however, if the ferric salt is first protected by conversion with ammonium phosphate into soluble complex ferric phosphate, quantitative formation of ferricyanide occurs on boiling with potassium cyanide. Ferricyanides are generally produced by oxidising ferrocyanides, either electrolytically or with chlorine or bromine. The transition from $Fe(CN)_6''''$ to $Fe(CN)_6'''$ can be reversed under suitable conditions of experiment. For instance ($X=Cl$ or Br)

$$2Fe(CN)_6''''+X_2 \rightleftharpoons 2Fe(CN)_6'''+2X'$$

(Gillet, Bull. Soc. chim. Belg. 1912, **26**, 236). In strongly acid solution under suitable conditions, potassium iodide is oxidised to iodine by ferricyanide, whilst in neutral solution ferrocyanide reduces iodine. Oxygen itself will oxidise ferrocyanide to ferricyanide in acid solution, but not in alkaline.

The commonest technical forms of ferrocyanide are "yellow prussiate of potash," $K_4Fe(CN)_6$, and Prussian blue (ferric ferrocyanide, etc.). Other ferrocyanides can be obtained from the potassium salt by double decomposition with metallic salts, and from Prussian blue by boiling with the hydroxides or carbonates of the alkali and alkaline earth metals, when solutions of the corresponding ferrocyanides are formed. Neither of these methods is entirely satisfactory for the production of pure compounds, for the products are usually contaminated by double salts which are formed with great ease and are not easily removed. If pure products are required, it is necessary to neutralise hydroferrocyanic acid with the appropriate base, or to treat barium ferrocyanide with the appropriate sulphate.

The ferrocyanides and ferricyanides of the alkali and alkaline earth metals are soluble in water, generally crystallising with water of crystallisation. The ferrocyanides are yellowish in the hydrated form, and almost white when anhydrous. The ferricyanides have a characteristic ruby-red colour. The heavy metal salts of both anions are generally insoluble amorphous precipitates, the ferrocyanides having characteristic colours which are not related to those of the component ions (*e.g.* cupric ferrocyanide is brownish-red, ferric ferrocyanide is deep blue), and this is held to indicate that a constitutional change occurs on their formation.

When heated above 400°C., the solid ferrocyanides are decomposed into the constituent cyanides, *e.g.* KCN and "$Fe(CN)_2$," the latter decomposing further into iron, carbon, iron carbide and nitrogen. Where one of the cyanides is volatile (*e.g.* NH_4CN or HCN), the primary decomposition, helped by the escape of the volatile product, occurs at a lower temperature. The solid ferricyanides undergo similar disruption on heating, and are less stable than the ferrocyanides, a loss of cyanogen being detectable even at 180°C. Complete disruption of the iron cyanide complex also occurs when the solid salts react with sulphuric acid: with dilute acid HCN is produced, and with concentrated acid the product is carbon monoxide, derived from HCN by its hydrolysis to ammonia and formic acid, the latter being subsequently dehydrated. In the case of ferricyanide, carbon dioxide also appears in the gaseous product, for the ferric salt arising from the initial disruption of the ferricyanide complex can oxidise some of the formic acid to carbon dioxide and water.

Ferrocyanide and ferricyanide solutions are electrolytically dissociated into metallic kations and iron cyanide complex anions. As already stated, the complex anions are very stable and give rise to no iron kations in solution. Under certain conditions, however, they are subject to a fission of one of the six cyanide groups, which is replaced by another group to form the complex pentacyanides. For instance, ferrocyanide solutions, on heating alone, on treating with acids, or by the action of light in the absence of acids, become alkaline and evolve HCN, forming aquopentacyanides in solution. The reaction, which is characterised by a yellowing of the ferrocyanide solution, is ionically represented as follows:

$$Fe(CN)_6'''' + 2H_2O = [Fe(CN)_5 \cdot H_2O]''' + OH' + HCN$$

A similar reaction occurs, but more readily, with ferricyanide solutions; in the presence of nitric acid the seceding cyanide group may be replaced by NO to give nitrosopentacyanide ("nitroprusside"), and with carbon monoxide carbonylpentacyanide is produced.

Ferrocyanides.

Technical Methods of Preparation. 1. *From Nitrogenous Organic Matter.*—The manufacture of ferrocyanides from nitrogenous organic matter by the process which led to the discovery of Prussian blue, and which was almost the sole source of ferrocyanide and cyanide until 1860, has now been entirely superseded and is only of historical interest. The forms of nitrogenous matter used were dried blood, horn, hair, waste wool and feathers, or the animal charcoal obtained by their destructive distillation. The material was fused with potassium carbonate and iron turnings in cast iron muffles or in reverberatory furnaces, and the melt was leached with hot water to obtain an aqueous solution from which potassium ferrocyanide crystallised out. The black insoluble residue from the leaching contained double sulphides of potassium and ferrous and ferric iron, and various double silicates of potassium, calcium and aluminium. The loss of potash in this residue appears to have been 45–90% of that usefully consumed.

The efficiency of ferrocyanide recovery in the process, based on the nitrogen content of the organic raw material, was very low. On direct fusion of the organic matter with potash, not more than 20% of the ferrocyanide theoretically obtainable was actually recovered (Karmrodt, Wagners Jahresber. 1857, **3**, 139). When the nitrogenous matter was first carbonised alone, about 80% of the nitrogen was lost in the escaping vapours as hydrocyanic acid, ammonia, and organic bases, and up to 57% of the nitrogen remaining in the charred mass was converted into ferrocyanide, corresponding to an overall yield of about 12%.

Although the reactions proceed equally well when sodium carbonate is substituted under appropriate conditions for potassium carbonate, the relatively poor crystallising properties of $Na_4Fe(CN)_6$.aq. make the isolation of the solid salt more difficult.

The probable mechanism of the ferrocyanide formation (Liebig, Annalen, 1841, **38**, 20) is that potassium cyanide is formed during the fusion by the action of potassium carbonate on the organic nitrogen compounds present in the charred material (*see* Kraemer, B.P. 16529 of 1894, who describes the production of cyanide by heating carbazole to redness with caustic potash), together with iron sulphides produced from the sulphur-containing bodies present in the organic material. Some iron sulphide may also be formed by reduction to sulphide of potassium sulphate present in the potash. For further details of the rôle of sulphur compounds in the fusion, the work of R. Hoffmann (Annalen, 1860, **113**, 81) may be consulted. The potassium cyanide and ferrous sulphide formed during the fusion react during the leaching to give potassium ferrocyanide:

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S$$

2. *From Coal Distillation Gases.*—The nitrogen content of bituminous coal varies widely, generally increasing with the geological age of the coal, but rarely exceeds 2%. The two types of coal which are subjected to distillation in practice are gas coal and coking coal. Gas coals generally contain from 1 to 2% of nitrogen, and nitrogen in various forms appears in all the products (coke, tar, gas liquor and gas) of distillation (Drehschmidt, J. für Gasbeleuchtung, 1904, 677; J. McLeod, J.S.C.I. 1907, **26**, 137). The distribution of the nitrogen between these products varies considerably, being influenced by the nature of the coal, its moisture content and the conditions under which the distillation is carried out. A general indication of the nitrogen distribution in the distillation products is given by the following collected data on the distillation of small samples of dry coal:

No.	Coal.	% of total N of the coal in				
		Coke.	NH_3	HCN	Tar.	As N_2 gas.
1	Durham .	48·7	14·5	1·6	—	35·2
2	Westphalia	50	12–14	1·8	1·5	30·0
3	—	48	15	2	—	35
4	Scottish .	58·3	17·1	1·5	3·9	19·5

1. Foster, J. of Gas Lighting, 1882, 1081.
2. Knublauch, J.S.C.I. 1896, **15**, 106.
3. Chief Inspector of Alkali Works, 43rd Report, 1906, 58.
4. J. McLeod, J.S.C.I. 1907, **26**, 137; Alkali Works, 44th Report, 1907, 215.

The yields of HCN quoted above are lower than those actually produced in large-scale working, a partial explanation being probably to be found in the fact that the experiments were carried out in retorts of iron, a metal which favours the decomposition of HCN at the distillation temperatures. A study of the numerous results of Drehschmidt (J. für Gasbeleuchtung, 1904, **47**, 677; *see also* Bertelsmann, "Technologie der Cyanverbindungen," Munich, 1906, p. 161) with English, Westphalian and Silesian coals does not disclose any connection between the nitrogen content of the coal and the distillation yield of HCN. On the other hand, as the water content of the coal (and the quantity of gas liquor obtained from it) increases, the yield of HCN decreases. This is due to the decomposition of HCN by steam at the distillation temperature into ammonia and carbon monoxide,

$$HCN + H_2O = NH_3 + CO$$

(Carpenter and Linder, J.S.C.I. 1905, **24**, 63). Thus the effect of the presence of 12% of moisture in a coking coal is to reduce by approximately one-third the amount of HCN present in coke oven gas as compared with town's gas made from dry coal.

As regards the effect of distillation conditions, increasing temperatures cause a transfer of nitrogen from the coke to the more volatile products, leading to an increase in the yields of ammonia, HCN and gaseous nitrogen. Ammonia may be regarded as a primary decomposition product of the coal substance, and HCN as a secondary product formed by the interaction of ammonia with carbon:

$$NH_3 + C \rightleftharpoons HCN + H_2.$$

This reaction is endothermic in the direction of HCN-formation, which is therefore favoured by higher temperatures (*see* Hydrocyanic Acid, p. 499). The following table shows the variation with temperature of the yields of ammonia and HCN obtained by O. Simmersbach (J.S.C.I. 1915, **34**, 895) with a Silesian coal containing 1·396% of nitrogen:

Temp. (°C.)	600	800	1,000	1,200
% of total nitrogen—				
as NH_3	7·81	21·28	23·15	22·84
as HCN	0·25	0·87	1·23	1·42

According to Bertelsmann ("Technologie der Cyanverbindungen," p. 168) the size and nature of the carbonisation chamber influence the production of HCN, the large and porous chambers of coke ovens being disadvantageous by comparison with the smaller, relatively gas-tight retorts of the gas works.

The gas leaving the distillation retorts contains ammonia, hydrogen sulphide, hydrocyanic acid (2–2·5 g. per cu. m.) and tar, and is first passed through coolers and scrubbers, the primary purpose of which is the removal of the ammonia and tar. In practice, however, considerable quantities of hydrogen sulphide and up to one-third of the hydrocyanic acid (depending on the amount of water used in the scrubbers) are also removed. This HCN appears as ammonium thiocyanate, and is ultimately discharged in the effluent from the ammonia stills; this effluent is sometimes worked up for thiocyanates, chiefly in England (Bertelsmann, *op. cit.* p. 180) *via* the cuprous and barium salts (*see* Thiocyanates, p. 508). The gas then passes to the iron oxide purifiers for complete removal of hydrogen sulphide, when 50–70% of the HCN is simultaneously taken up. This cyanide can be recovered by suitably treating the spent mass as described below (Dry Process). A more recent method of cyanide recovery from coal gas, giving greater efficiency, is the use of special cyanide washers, generally before the ammonia scrubbers (Wet Process).

(*a*) *Dry Process.*—The gas purification mass consists either of precipitated ferric hydroxide mixed with sawdust to increase the porosity, or of natural iron ores. The first technically successful mass was introduced by Laming (B.P. 11944 of 1847), and was made by mixing ferrous sulphate with slaked lime and sawdust and oxidising the damp mass in air. The use of natural ores was introduced by Howitz in 1870. The mass absorbs hydrogen sulphide from the gas, forming ferrous and ferric sulphides and elementary sulphur, and takes up HCN to form Prussian blue and ammonium thiocyanate. When saturated with respect to hydrogen sulphide, the mass is regenerated by dampening and exposing to air, the ferrous and ferric sulphides being oxidised to ferric hydroxide and sulphur. With successive regenerations the sulphur and cyanide contents of the mass increase until it is no longer effective as a purifying agent.

The air-dried "spent oxide" is a dirty greenish, friable substance smelling strongly of ammonia and organic sulphur compounds, and generally containing up to 50% of free sulphur and 10–14% of Prussian blue, except that the blue content does not rise above 4% when a cyanide washer has been used. This latter material is not considered attractive as a source of ferrocyanide, the minimum content at which spent oxide is saleable for ferrocyanide recovery being about 7%. Ammonium thiocyanate may be present in quantities varying from traces up to 10%. The ferrocyanide in spent oxide is formed from the ferrous hydroxide and ammonium cyanide, and is then converted into Prussian blue by interaction with the ferric iron. Ammonium thiocyanate is formed from hydrocyanic acid and ammonium polysulphide, the latter obviously arising from the presence of ammonia, hydrogen sulphide, and sulphur in the purifier; the formation of thiocyanate is favoured by raising the temperature, as occurs if the mass is regenerated quickly.

The different methods adopted for the treatment of the spent oxide are all variants of the following general procedure. The soluble ammonium salts (chiefly sulphate and thiocyanate) are removed from the screened mass by systematic leaching with cold water for 14–24 hours, and the residue is dried. At this stage the elementary sulphur may be removed by solvent extraction, for example, with carbon bisulphide. This step is technically advantageous, since it minimises the formation of unwanted thiocyanate at a later stage, but is economically unsound owing to the fact that the sulphur recovered is contaminated with tar which can only be removed with great difficulty. The dry mass is then mixed in thin layers with the calculated amount of powdered slaked lime to decompose the Prussian blue content, the mixture warmed to drive off the last retained traces of ammonia, and then leached with water. An impure solution of calcium ferrocyanide is produced, from which the sodium or potassium salt may be obtained by decomposition with the corresponding carbonate, filtering off the precipitated calcium carbonate and crystallising the solution. On the other hand, a Prussian blue may be directly precipitated from the impure solution by acidifying with hydrochloric acid, removing the precipitate of sulphur thus formed, and adding ferrous or ferric salt solution, and the precipitated blue converted into potassium ferrocyanide by boiling with caustic potash and evaporating the solution: this lengthy and expensive process is now used only for ferrocyanide recovery from mother liquors and wash waters obtained in the process to be described below.

Two improved methods of working up the impure calcium ferrocyanide solution were described by Kunheim and Zimmermann (B.P. 3342 of 1883), and are now generally used. In the first, the sparingly soluble double salt $K_2CaFe(CN)_6$ is separated by the addition to the hot, concentrated solution (at 80°C.) of the calculated amount of potassium chloride with constant stirring. The solid is filtered off and washed with a limited quantity of water; the filtrate and washings are worked up for potassium ferrocyanide *via* Prussian blue by the method described above. The crystalline double salt is treated with the calculated amount of potassium carbonate solution at the boiling-point, when calcium carbonate separates. The clear potassium ferrocyanide solution is left to crystallise for 14 days, and gives directly a pure product. In addition to the purity of the product, this process has the advantage that one-half of the calcium replacement is achieved with the cheaper potassium chloride instead of potassium carbonate. The second improved method makes use of the sparing solubility of the calcium ammonium double salt; in this case, sufficient ammonia is allowed to pass the ammonia scrubber in the gas purification to ensure that the double salt $Ca(NH_4)_2Fe(CN)_6$ is precipitated from the leaching solution on neutralising with hydrochloric acid. This salt is then decomposed with lime to give a pure calcium ferrocyanide solution, which is filtered and treated by the KCl-K_2CO_3 process already described. The product is very pure.

(*b*) *Wet Process.*—The wet process of cyanide removal first came into successful practical operation in 1895, and is now an important source of ferrocyanides. It has several advantages over the dry process. The absorption of HCN in purifier boxes is an involuntary adjunct to the main purpose of sulphur removal, and the removal of HCN is not complete. The cyanide scrubber, on the other hand, provides a controlled method of cyanide removal which works at an efficiency of nearly 100%; and the recovery of ferrocyanide from "cyanide mud" is considerably easier than from spent oxide. It is also stated that the working efficiency of oxide boxes for H_2S removal is greater with gas which has already passed through a cyanide washer, and that the spent oxide produced from such a gas is more suitable for sulphuric acid manufacture (Drory, J. für Gasbeleuchtung, 1903, **46**, 143).

The first practical absorbent to be proposed was a suspension of ferrous hydroxide in an alkali carbonate solution (Knublauch, B.P. 15164 of 1887, Ber. 1888, **21**, 208), but the process did not meet with commercial success. Foulis (B.P. 9474 of 1892) substituted for ferrous hydroxide in the slurry a partially oxidised basic ferrous carbonate, the reagent being made by precipitating a ferrous salt solution with sodium carbonate, washing the precipitate and suspending it in sodium carbonate solution. This washing medium has achieved commercial success when used in a rotary washer designed to handle slurries (Foulis and Holmes, B.P. 15168 of 1895). When the cyanide washer is placed after the ammonia scrubber, the absorbed cyanide appears in the form of soluble sodium ferrocyanide, which is recovered by evaporating the solution after filtering off the suspended solids. A modified method of operation, practised at the Hague gas works, was described by Rutten (J. of Gas Lighting, 1902, **80**, 875) and by Jorissen and Rutten (J. für Gasbeleuchtung, 1903, **46**, 716): the crude gas, after tar separation, is passed through the cyanide washer before going to the ammonia scrubber, and a 20% increase in the cyanide recovery results, both soluble and insoluble ferrocyanides being formed. The saturated liquor from the washer, containing Prussian blue, potassium and ammonium ferrous ferrocyanides in suspension, and ammonia and potassium ferrocyanides in solution, is filter-pressed, and the filtered solution distilled to separate ammonia and then evaporated *in vacuo* to crystallisation. The press-cake is boiled with caustic potash and the ammonia collected, the iron oxide being returned to the cyanide washer and the solution of ferrocyanide proceeding to the evaporation plant.

The ammonia present in the gas may itself be used as the alkali and the crude gas be simply washed with a ferrous sulphate solution. In this case, ammonia and hydrogen sulphide present in the gas give ammonium sulphide, so that the wash liquor is quickly converted into a suspension of ferrous sulphide in ammonium sulphate solution: the ferrous sulphide subsequently reacts with ammonium cyanide in solution. Earlier processes of this kind (Rowland, B.P. 22347 of 1891; Lewis and Cripps, B.P. 20883 of 1896; Schröder, B.P. 19849 of 1898; Teichmann, B.P. 12485 of 1899) used dilute ferrous salt solutions so that ammonia was always present in excess, with the object of obtaining ferrocyanide wholly in the soluble form. Bueb, on the other hand (B.P. 9075 of 1898), almost completely avoids the formation of soluble salts by using a saturated ferrous sulphate solution, maintaining ferrous iron in permanent excess in the solution and producing ferrocyanide in the insoluble form. This process is widely used, and is said to absorb 98% of the hydrocyanic acid in the gas to give a mud containing the equivalent of 18–20% of $K_4Fe(CN)_6$ (Bueb, J. für Gasbeleuchtung, 1900, **43**, 747). The mud is treated with some ferrous sulphate solution to convert small quantities of soluble ammonium ferrocyanide into insoluble ferrocyanide, and then with steam to remove ammonia. It is then dried in filter presses and the cake, containing the equivalent of 40% of $K_4Fe(CN)_6$, is converted into calcium ferrocyanide solution by boiling with milk of lime. The clarified solution is then converted into potassium ferrocyanide by the method of Kunheim and Zimmermann already described.

The mechanism of ferrocyanide formation in the wet absorption of cyanide from coal gas, and an explanation of the effect of the variation of the conditions on the form in which the product appears, have been given by Feld (J. für Gasbeleuchtung, 1904, **47**, 132). He considers that the basic reaction is between ammonium cyanide and ferrous sulphide, formed in the way previously explained. If ferrous sulphide is present in excess, insoluble ferrous ferrocyanide is the main product; under more balanced conditions, insoluble ammonium ferrous ferrocyanide is formed in increasing quantities, and when there is a deficiency of ferrous sulphide, the soluble ammonium ferrocyanide is produced.

3. *From Thiocyanates.*—Many processes have been described for the conversion of thiocyanates, which are formed in various methods of cyanide synthesis and in gas purification, into the more valuable ferrocyanides. The processes consist essentially in a desulphurisation with metallic iron, and may be carried out with the molten salts or their solutions. Alexander (J. für Gasbeleuchtung, 1878, **21**, 20) described a method in which ammonium thiocyanate, potassium carbonate, carbon, and iron filings are rubbed to a paste with oil and heated in a closed iron vessel to red heat. The reaction product is leached with an aqueous suspension of freshly precipitated ferrous hydroxide, and the filtrate evaporated to crystallisation. Tscherniac and Gunzburg (B.P. 1261 of 1881, *see also* 1148 of 1878 and 1359 of 1879) and Hetherington and Muspratt (B.P. 5830 of 1894) used a 20–30% excess of reduced iron and molten potassium thiocyanate which had been dried at 300°C., the reaction temperature being 445°C. Crowther, Rossiter, Hood and Albright (B.P. 8305 of 1894) recommend drying the thiocyanate in a stream of nitrogen or carbon dioxide. In laboratory experiments on Hetherington's method, Conroy (J.S.C.I. 1896, **15**, 12) obtained a 77% conversion of thiocyanate to ferrocyanide. The mechanism of the reaction is analogous to that of ferrocyanide formation from nitrogenous organic matter, viz. cyanide and ferrous sulphide are formed during the fusion, and react to give ferrocyanide during the leaching.

The desulphurisation may be carried out in solution by the method of Sternberg (G.P. 32892 of 1882), by heating a solution of potassium thiocyanate with twice the theoretical weight of iron filings necessary for sulphide formation and twice the theoretical weight of ferrous hydroxide necessary for ferrocyanide formation, at 110–120°C. under pressure. In 12 hours a conversion of 80% is obtained. Conroy (J.S.C.I. 1898, **17**, 98) used a mixture of calcium thiocyanate and ferrous chloride and iron in water at 140–150°C. to increase the rate of reaction:

$$\begin{aligned}&Ca(CNS)_2+2Fe+FeCl_2\\&\qquad\qquad CaCl_2+Fe(CN)_2+2FeS\end{aligned}$$

The mud is treated with hydrochloric acid to dissolve ferrous sulphide, and the ferrous ferrocyanide boiled with alkali to form soluble ferrocyanide.

Copper (Bower, B.P. 361 of 1896) or nitric acid may be used as desulphurising agents (*see* Hydrocyanic Acid, p. 492).

4. *From Cyanides.*—The fact that the conversion of synthetic cyanides into ferrocyanides is becoming a technical process displacing the recovery of by-product ferrocyanide at gas works, especially in the United States, indicates the change in the relative economy of cyanides and ferrocyanides which was caused by the introduction of cyanide synthesis processes from ammonia and from nitrogen. The technical conversion of cyanide to ferrocyanide is brought about by the action of cyanide solution on iron, iron sulphide or ferrous salt. The chief source of cyanide for this purpose is the crude calcium cyanide (analysing 45% $Ca(CN)_2$, 32% $NaCl$) obtained on fusing technical calcium cyanamide with sodium chloride (*see* Alkaline Earth Cyanides, p. 488). This is dissolved in water and treated with the calculated amount of ferrous sulphate to satisfy the requirements of the reaction equation

$$3Ca(CN)_2+FeSO_4=CaSO_4+Ca_2Fe(CN)_6,$$

and with slightly less than the amount of sodium carbonate equivalent to the ferrocyanide produced:

$$\begin{aligned}&Ca_2Fe(CN)_6+2Na_2CO_3\\&\qquad\qquad =Na_4Fe(CN)_6+2CaCO_3.\end{aligned}$$

The sodium ferrocyanide in solution is separated from the sodium chloride by crystallisation (Washburn, U.S.P. 1398453, 1921; Rugh, U.S.P. 1650390, 1927).

The American Cyanamid Co. (U.S.P. 1667839, 1928) proposes to make the slightly soluble calcium potassium ferrocyanide by a similar reaction after addition of potassium chloride. The straightforward interaction of sodium cyanide (the commonest synthetic cyanide) with ferrous sulphate presents some difficulty in the separation of the two soluble products, sodium ferrocyanide and sodium sulphate. According to Dominik (*see* Chem. Zentr. 1923, IV, 494), the solubility relations are such that sodium sulphate is retained in solution on evaporation above 32°C. For the conversion of sodium ferrocyanide into the potassium salt, which is sometimes required, it is necessary to add to the hot solution a considerable excess of potassium chloride and to cool to crystallisation

(Conroy, J.S.C.I. 1898, **17**, 98; Petri, G.P. 212698, 1909).

Instead of using calcium cyanide made from cyanamide, the Strontian- und Potasche-Fabrik (G.P. 330194, 1920) describe a method of converting cyanamide directly into ferrocyanide by heating it to redness with potassium carbonate and iron shavings in the absence of air.

Properties of the Ferrocyanides.—In this section the principal characteristics are described of those salts which possess technical interest. For further information, "Cyanogen Compounds" by H. E. Williams (1915) or an "Inorganic Chemistry" *e.g.* Mellor's should be consulted.

Ammonium ferrocyanide is prepared in aqueous solution from the free acid and ammonia, from barium ferrocyanide and ammonium sulphate, or from lead ferrocyanide and ammonium carbonate. The solid salt, $(NH_4)_4Fe(CN)_6,3H_2O$, is obtained by evaporating the solution *in vacuo* (Briggs, J.C.S. 1911, **99**, 1019), or by precipitation with alcohol (Cumming and Good, J.C.S. 1926, **129**, 1924). The salt crystallises with difficulty in very pale yellow plates, isomorphous with the potassium salt (Bunsen, Pogg. Ann. 1835, **36**, 404). When $(NH_4)_4Fe(CN)_6$ is heated *in vacuo*, decomposition begins at 110°C., NH_4CN being evolved (Mittasch, Kuss and Emert, Z. anorg. Chem. 1928, **170**, 193); at 320°C., "$Fe(CN)_2$" remains behind, which begins to evolve nitrogen at 430°C.; and at 700°C. a mixture of iron, iron carbide and nitride remains. When the heating is carried out in an atmosphere of hydrogen, methane and ammonia are formed and the residue is pure iron. The aqueous solution decomposes on boiling to give ammonium cyanide and an insoluble residue possibly consisting of partly oxidised ammonium ferrous ferrocyanide.

From solutions containing much ammonium chloride a double salt,

$$(NH_4)_4Fe(CN)_6{\cdot}2NH_4Cl,3H_2O,$$

crystallises readily in well-formed orange-yellow rhombohedra, which were formerly mistaken for the ammonium salt (Bunsen, *l.c.*).

Barium ferrocyanide, $Ba_2Fe(CN)_6,6H_2O$, is precipitated on mixing strong solutions of barium chloride and sodium ferrocyanide (Ewan and Napier, J.S.C.I. 1913, **32**, 467) as a light yellow, crystalline powder. The preparation of pure barium salt from $K_4Fe(CN)_6$ is difficult, as the product generally contains potassium; Walker (J. Amer. Chem. Soc. 1895, **17**, 927) avoided the difficulty by first making the dimethylaniline salt and decomposing this with barium hydroxide, extracting the liberated dimethylaniline with ether. The dried salt, heated *in vacuo* or in nitrogen, begins to decompose at about 500°C., giving nitrogen, carbon, iron, and barium cyanide and cyanamide. When oxygen is completely excluded, the molecular ratio of cyanamide to cyanide in the product is 2 : 1 (Ewan and Napier, *l.c.*). The solubility of the salt in water, expressed as g. of anhydrous salt in 100 g. of water, is 0·34 at 15·5°C. and 1·01 at 100°C. More than 5 molecules of water of crystallisation are relatively easily removed by heating to 80°C. for a few hours, but the remainder is not completely given up, even at 180°C. (Ewan and Napier, *l.c.*).

Barium potassium ferrocyanide,

$$BaK_2[Fe(CN)_6],3H_2O \text{ or } 5H_2O,$$

is precipitated as a pale yellow, crystalline powder on mixing equivalent quantities of dilute solutions of barium chloride and potassium ferrocyanide. The crystals effloresce readily, a property which accounts for the uncertainty as to the amount of water of crystallisation. The solubility in water (g. of anhydrous salt in 100 g. of water) is 2·1 at 15·5°C. and 6·08 at 100°C.

Calcium ferrocyanide,

$$Ca_2Fe(CN)_6,11H_2O,$$

is made by treating Prussian blue with milk of lime, neutralising hydroferrocyanic acid with calcium carbonate, or from potassium ferrocyanide *via* the dimethylaniline salt (*see* Barium Ferrocyanide, above). The crystals were formerly believed to contain $12H_2O$, but more recent work (Berkeley, Hartley and Burton, Phil. Trans. 1909, **209**, (A), 177; Cumming, J.C.S. 1924, **125**, 240; Farrow, *ibid.* 1926, **129**, 49; 1927, 1153) favours $11H_2O$. The salt is extremely soluble in water (*cf.* the barium salt), giving viscous solutions at high concentrations. The crystals effloresce and lose all but ½ molecule of water at 40°C. Cumming (*l.c.*) detected some hydrolysis to give a compound $Ca_4Fe_2(CN)_{11}OH$ on heating at 100°C. in a current of oxygen-free gas. At 500°C. in the absence of oxygen, Pincass (Chem.-Ztg. 1922, **46**, 661) observed a decomposition to give calcium cyanamide:

$$Ca_2Fe(CN)_6 = 2CaCN_2 + Fe + N_2 + 4C$$

Calcium ammonium ferrocyanide,

$$Ca(NH_4)_2Fe(CN)_6,$$

may be prepared from calcium chloride and ammonium ferrocyanide solutions, and forms a white, minutely crystalline powder, containing no water of crystallisation, which becomes coloured on exposure to light. 100 g. of water at 15–17°C. dissolve 0·258 g. of the salt (J. Campbell Brown, J.C.S. 1907, **91**, 1826). The insolubility of the salt is used in separating ferrocyanide from gas purification mass.

Calcium potassium ferrocyanide,

$$CaK_2Fe(CN)_6,$$

is made from calcium chloride and potassium ferrocyanide solutions, forming a white powder of small quadratic prisms which are anhydrous and discolour slightly on exposure to light. At 15–17°C. the solubility is 0·41 g. per 100 g. of water (J. Campbell Brown, *l.c.*).

Cupric ferrocyanide, $Cu_2Fe(CN)_6.aq.$, can be prepared either from cupric salt and ferrocyanide, or from cuprous salt and ferricyanide, for the ionic oxidation-reduction equilibrium

$$Cu^{++} + Fe(CN)_6'''' \rightleftharpoons Cu^{+} + Fe(CN)_6'''$$

is almost completely to the left (Müller, Wegelin and Kellerhoff, J. pr. Chem. 1912, [ii], **86**, 82)

The usual method of preparation is by the addition of a solution of calcium ferrocyanide or hydroferrocyanic acid to an excess of cupric chloride, and the product is a red-brown, amorphous substance containing varying amounts of water. It is very slightly soluble in water and dilute acids, but can be brought into colloidal solution by means of peptising agents, particularly through the agency of ferrocyanide ions adsorbed from solutions. The brown precipitate formed when cupric salts react with potassium ferrocyanide (Hatchett's brown, formerly used as a pigment) always contains potassium, even when cupric copper is present in excess, and this may be explained either by adsorption of $K_4Fe(CN)_6$ by the solid $Cu_2Fe(CN)_6$ (Luckow, Chem.-Ztg. 1892, **16**, 164, 836, 1428; Duclaux, Compt. rend. 1904, **138**, 144, 571) or by the formation of a double salt (*e.g.* $CuK_2[Fe(CN)_6],2H_2O$, Reihlen and Zimmermann, Annalen, 1927, **451**, 75). Colloidal membranes of copper ferrocyanides have been used extensively in the study of osmosis, and copper ferrocyanide finds application in photography for toning : the black deposit of silver in a bromide print is converted into a red one, consisting of copper ferrocyanide, by immersion in a solution of copper sulphate, potassium ferricyanide, and potassium citrate (Ferguson, Phot. J. 1900, 133).

Reihlen and Zimmermann (Annalen, 1927, **451**, 75) regard cupric ferrocyanide as the copper salt of a complex anion containing both copper and iron ; for on boiling with milk of lime it gives brown crystals of $Ca[CuFe(CN)_6]$, and with dilute ammonia it gives the salt $[Cu(NH_3)_4][CuFe(CN)_6]H_2O$; such reactions indicate that one-half of the copper in cupric ferrocyanide is in the complex ion.

Cuprous ferrocyanide is not known in the simple form, but the existence of the double salts $KCu_3Fe(CN)_6$ and $K_2Cu_2Fe(CN)_6$ has been indicated by Müller, Wegelin and Kellerhoff (J. pr. Chem. 1912, [ii], **86**, 82), using the method of indirect analysis described later. Messner (Z. anorg. Chem. 1895, **8**, 368) describes the preparation of $K_2Cu_2Fe(CN)_6$ by the action of cuprous cyanide or cuprous chloride, in the presence of potassium sulphite to prevent oxidation, on potassium ferrocyanide solution, the mixture being quickly cooled to obtain the double salt in the form of colourless plates. It appears likely that, in the above double salts, the copper is part of the complex ion (Reihlen and Zimmermann, Annalen, 1927, **451**, 75). The cuprous ferrocyanide compounds differ from other ferrocyanides in evolving the whole of their cyanogen as hydrocyanic acid on boiling with dilute sulphuric acid (*see* Dewrance and Williams, B.P. 28074 of 1908).

Hydroferrocyanic acid, $H_4Fe(CN)_6$, may be prepared by the decomposition of a suspension of the lead salt with sulphuric acid and evaporation of the filtrate, or by treating a concentrated solution of potassium ferrocyanide with excess of concentrated hydrochloric acid, preferably with addition of ether (*see*, for example, Mittasch and Kuss, Z. Elektrochem. 1928, **34**, 159). The acid crystallises in colourless scales which are washed with water saturated with ether, and dried over sulphuric acid. It may be purified by dissolving in alcohol and precipitating with ether; it obstinately retains ether, with which it forms a compound (*see*, for example, Cumming and Brown, J.S.C.I. 1928, **47**, 84T), and must be heated to 100°C. in a stream of dry hydrogen to free it completely (Browning, J.C.S. 1900, **77**, 1234). Heated in the absence of oxygen, the acid begins to decompose at 150°C. into HCN and "$Fe(CN)_2$." The solubility of the acid in water at 14°C. is 13 g. per 100 g. of solution. The solution is readily oxidised by air at higher temperatures, forming a blue substance which is assumed to be Prussian blue; this reaction is used in calico printing for the production of blue patterns.

Ferrous ammonium ferrocyanide,

$Fe(NH_4)_2[Fe(CN)_6]$,

is formed when ammonium ferrocyanide solution is exactly precipitated by a ferrous salt in the presence of an excess of an ammonium salt, oxygen being excluded. It is also formed when ammonium ferrocyanide is distilled with an acid in the absence of air.

Ferrous potassium ferrocyanide,

$K_2Fe[Fe(CN)_6]$,

(*Everitt's salt*) is produced by heating saturated potassium ferrocyanide solution for 40 hours at 90°C. with an equal volume of 20% sulphuric acid, washing and drying the residue with exclusion of air (Hofmann, Heine and Höchtlen, Annalen, 1904, **337**, 1). The pale yellow product is not oxidised by air, and is therefore different from the isomeric salt obtained when solutions of potassium ferrocyanide and ferrous chloride are mixed (Hofmann, *l.c.*). For this reason Reihlen and Zimmermann (Annalen, 1927, **451**, 75) formulate it as $K_2[Fe_2^{II}(CN)_6]$.

Iron cyanide blue compounds.—The blue compounds of iron and cyanogen may be prepared by the interaction of ferric salts with ferrocyanides, or of ferrous salts with ferricyanides, in neutral or acid solution. The constitution of these compounds is discussed in greater detail on p. 473, but it may be stated here that they are believed to be ferric ferrocyanides. Müller has shown that the composition of the unwashed precipitate initially formed depends on the relative quantities of reagents employed (Chem.-Ztg. 1914, **38**, 281, 328). Starting from potassium ferrocyanide and ferric chloride, Prussian blue is precipitated when the molar ratio $K_4Fe(CN)_6/FeCl_3$ is less than 0·75 ; for values between 0·75 and 0·92 the precipitate contains increasing quantities of $KFe^{III}[Fe^{II}(CN)_6]$, and when the ratio exceeds 0·92 the substance $K_2Fe^{II}[Fe^{II}(CN)_6]$ is also present. Starting from potassium ferricyanide and ferrous chloride, a precipitate of the composition $KFe_2^{II}Fe_5{}^{III}[Fe^{II}(CN)_6]_5$ is obtained when the molar ratio $K_3Fe(CN)_6/FeCl_2$ is less than 0·714; between 0·714 and 0·75 a substance $KFe^{II}Fe_3{}^{III}[Fe^{II}(CN)_6]_3$ is formed, which Müller regards as ordinary *Turnbull's blue*; from 0·75 to 0·9 increasing quantities of $KFe^{III}[Fe^{II}(CN)_6]$ are present, and finally, when the ratio exceeds 0·9 ordinary Prussian blue, $Fe_4{}^{III}[Fe^{II}(CN)_6]_3$, appears.

Blue compounds are also obtained by the oxidation of ferrous ferrocyanide, and by the reduction of ferric ferricyanide. All the blue compounds are amorphous substances containing indefinite quantities of water, some of which is so tenaciously retained as to be regarded as water of constitution. Their colour depends on the composition, water content, and particle size, and varies from pure blue to deep violet blue, a coppery metallic surface reflection being sometimes also present. They do not form true solutions in water. The so-called "soluble blues" give deep blue colloidal solutions with pure water, from which they can be precipitated by the methods normally effective with colloidal solutions. "Insoluble blues" are not peptised in pure water, but only in oxalic acid solution, and sometimes in acid or neutral oxalates and tartrates.

The blue compounds are quite stable towards dilute acids. Concentrated hydrochloric and sulphuric acids dissolve them with decomposition, giving ferrous or ferric salt and hydroferro- or hydroferri-cyanic acid; the blue may be re-formed on diluting the solution. They are coagulated by alcohol. Alkalis, or salts with an alkaline reaction, decompose them to give iron hydroxide and ferrocyanide, the rate of decomposition varying with the different compounds and providing a method of distinguishing them. Colloidal solutions of Prussian blue (0·2 to 2%) are negatively charged, the blue being coagulated by kations, especially hydrogen ion.

The characterisation of different blues by analysis is difficult. Simple analytical methods are useless because the colloidal nature of the blues gives them the property of strongly adsorbing dissolved salts from solution, and renders the usual methods of purification generally impracticable. In addition, some blue compounds, which contain ferrous iron outside the complex radicle, are easily oxidised by atmospheric oxygen, so that changes of composition may occur during the manipulation of the original product, unless special precautions are taken. For this reason, the indirect method of analysis, by which the composition of a precipitate is determined by mixing known quantities of the reagents and estimating the excess left in the supernatant liquid, has been used by Müller and his school (Müller and Stanisch, J. pr. Chem. 1909, [ii], **79**, 81; 1909, [ii], **80**, 153; Müller, Wegelin, Treadwell and Diefenthaler, *ibid.* 1911, [ii], **84**, 353; Müller, *ibid.* 1914, [ii], **90**, 119) and by Woringer (*ibid.* 1913, [ii], **87**, 51), although the objection still holds that the precipitate is not a pure substance on account of adsorption.

A description will now be given of the more important types of blue compounds, the data referring in each case to the solids obtained after exhaustive drying of the original precipitates with phosphorus pentoxide. Our knowledge of these compounds is largely based on the work of Hofmann and his collaborators (Hofmann, Heine and Höchtlen, Annalen, 1904, **337**, 1; Hofmann and Resenscheck, *ibid.* 1905, **340**, 267; 1905, **342**, 364; Hofmann, Arnoldi and Hiendlmaier, *ibid.* 1907, **352**, 54). The blue compounds are now formulated either as salts of hydroferrocyanic acid, $H_4[Fe^{II}(CN)_6]$, or as salts of a hydro-ferro-ferricyanic acid,

$$H[Fe^{II}Fe^{III}(CN)_6]$$

(*see* Constitution of the Blue Compounds, p. 473), and in the following section the formulæ for both systems are quoted.

Soluble Prussian blue,

$$KFe^{III}[Fe^{II}(CN)_6]aq. \text{ or}$$
$$K[Fe^{II}Fe^{III}(CN)_6]aq.,$$

is formed when cold neutral solutions of potassium ferrocyanide and ferric chloride are mixed, the ferrocyanide being in excess; the precipitate is washed with aqueous alcohol to free it from electrolyte, and dried *in vacuo* over sulphuric acid or phosphorus pentoxide. The same substance is also formed by adding cold neutral ferrous salt to an excess of potassium ferricyanide solution, and similarly treating the precipitate (Skraup, Annalen, 1877, **186**, 371; Hofmann, Heine and Höchtlen, Annalen, 1904, **337**, 1). The water content of the dried substance is variously reported as up to $4H_2O$, of which 2 molecules cannot be removed without decomposition, and are therefore regarded as constitutional. The substance is soluble in water, giving a colloidal solution which is coagulated by adding strong electrolytes or acids, and by alcohol. It is also soluble in oxalic acid solution.

Substances of similar composition and but slightly different properties are obtained by treating ferrous sulphate solution with potassium ferrocyanide, and oxidising the white ferrous ferrocyanide produced, either with atmospheric oxygen or with hydrogen peroxide. When this is done in neutral solution, the product,

$$KFe^{III}[Fe^{II}(CN)_6],H_2O,$$

is soluble in water, but not in oxalic acid solution and is immediately decomposed by ammonia solution (Hofmann). When the preparation is carried out in the presence of 1% of sulphuric acid, on the other hand, it yields an isomeric blue compound which is soluble in water and in oxalic acid solution, but is more stable towards ammonia solution, requiring 6–7 minutes for the precipitation of ferric hydroxide.

A soluble blue containing ammonium instead of potassium (*Monthier's blue*) can be obtained by oxidising ferrous ammonium ferrocyanide with air or hydrogen peroxide.

Insoluble Prussian blue,

$$Fe_4^{III}[Fe^{II}(CN)_6]_3aq. \text{ or}$$
$$Fe^{III}[Fe^{II}Fe^{III}(CN)_6]_3aq.,$$

can be made by decomposing cold neutral or slightly acid potassium ferrocyanide solution with excess of ferric salt, washing the precipitate with dilute hydrochloric acid and drying it *in vacuo*. It is also produced from soluble Prussian blue by digesting with ferric chloride solution:

$$3K[Fe^{II}Fe^{III}(CN)_6]+FeCl_3 = Fe^{III}[Fe^{II}Fe^{III}(CN)_6]_3+3KCl;$$

by oxidising ferrous ferrocyanide in the presence of excess ferrous salt; and by oxidising insoluble Turnbull's blue, a compound containing ferrous iron outside the complex radicle (*see below*) (Müller, Chem.-Ztg. 1914, **38**, 281, 328). The water content of the product varies considerably according to the treatment during preparation, but after long drying *in vacuo* over phosphorus pentoxide reaches a lower limit of $10\text{–}11H_2O$ (Hofmann, Heine and Höchtlen, Annalen, 1904, **337**, 1). Further dehydration by heating above 150°C. is accompanied by decomposition. Insoluble Prussian blue does not give colloidal solutions with pure water, but only with oxalic acid, oxalate and tartrate solutions.

Oxidising agents such as chlorine and nitric acid frequently give rise to green solutions and green precipitates ("Prussian green"), which are believed to be complex mixtures intermediate in composition between ferric ferrocyanide and ferric ferricyanide.

Insoluble Turnbull's blue,

$$Fe^{II}Fe_2^{III}[Fe^{II}(CN)_6]_2\text{aq. or}$$
$$Fe^{II}[Fe^{II}Fe^{III}(CN)_6]_2\text{aq.,}$$

is produced by precipitating a solution of potassium ferricyanide with excess of ferrous salt, or by treating soluble Prussian blue with ferrous salt:

$$2K[Fe^{II}Fe^{III}(CN)_6]+FeCl_2 = Fe^{II}[Fe^{II}Fe^{III}(CN)_6]_2+2KCl.$$

It is formed by the reduction of insoluble Prussian blue with ferrous ion or sulphite (Müller, J. pr. Chem. 1914, [ii], **90**, 119). The water content of Turnbull's blue is variously reported. The blue is colloidally soluble in oxalic acid solution, but not in water. Moderate oxidation, or reaction with ferric salts, gives insoluble Prussian blue:

$$3Fe^{II}[Fe^{II}Fe^{III}(CN)_6]_2+2FeCl_3 = 2Fe^{III}[Fe^{II}Fe^{III}(CN)_6]_3+3FeCl_2$$

Williamson's blue or violet,

$$KFe^{III}[Fe^{II}(CN)_6].H_2O,$$

is obtained by the oxidation of Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$ with warm dilute nitric acid, or with an excess of hydrogen peroxide in the presence of dilute sulphuric acid (Hofmann, Heine and Höchtlen, Annalen, 1904, **337**, 1). It is a violet-blue substance, not peptisable in water or in oxalic acid solution, giving only a greenish-blue turbid suspension with water. It is relatively unreactive, giving ferric hydroxide with 4% ammonia solution, for instance, only after some hours. It is thus entirely different from the isomeric blues obtained by oxidising ferrous ferrocyanide (*see* Soluble Prussian Blue, *above*). It is a general rule that the precipitation of blues from hot acid solutions tends to produce substances of a more stable type, approaching Williamson's blue in properties.

Commercial blues are usually mixtures of the compounds already described, and appear in commerce under such names as ***Paris blue bronze blue*** and ***steel blue*** (mostly containing potassium, and of superior properties), ***Prussian blue*** and ***mineral blue*** (less valuable products consisting of mixtures), and ***gas blue*** or ***Monthier's blue*** (containing ammonia). Of the three methods of manufacture, the reaction of ferrous salts with ferricyanide (formation of Turnbull's blue) has been discontinued, and the reaction of ferric salts with ferrocyanide (formation of Prussian blue) is rarely practised. The best blues are made by precipitating a ferrous salt with potassium ferrocyanide and then oxidising the precipitate (Gentele, "Lehrbuch der Farbenfabrikation," 1906). Paris blue, the finest quality of commercial Prussian blue, may be made by mixing 45 kg. of $FeSO_4,7H_2O$ (a slight excess), dissolved with exclusion of air in 250 kg. of water, with 50 kg. of $K_4Fe(CN)_6$ dissolved in the same quantity of water, and running the mixture into a further quantity of 250 kg. of water. The precipitate is washed and filtered off to be oxidised by suspending it in water, dilute sulphuric acid or ferrous sulphate solution and treating it with nitric acid of sp.gr. 1·23, ferric chloride solution (not in excess), chlorine, or potassium chlorate solution. The precipitate of Prussian blue is then washed with water until free from sulphate or chloride, filtered and air-dried at 30–40°C. Chlorate is now said to be the preferred oxidising agent (Itzkovich and Shmul'yan, *see* Amer. Chem. Abstr. 1934, **28**, 3997).

Paris blue contains potassium ferric ferrocyanide, and the presence of the potassium leads to an enhancement of the properties of the blue. If sodium is present instead (by making the preparation from sodium ferrocyanide) a less satisfactory colour is produced. Eibner and Gerstacker (J.S.C.I. 1912, **31**, 1041) measured the potassium and water contents of a number of blues: steel blue and bronze blue contained 12% K and 5·5% H_2O, Paris blue 9% K and 10·5% H_2O, commercial Prussian blue 1·5% K and 24% H_2O. The rise of water content as the potassium content falls is marked, and may be explained as an effect of the electrolyte (potassium ion) in "salting out" the colloid and reducing the water absorption.

In commercial pigments, Paris blue is diluted with finely ground starch, heavy spar, gypsum, zinc white or burnt kaolin, and the mixture milled. Blues of very low quality are faced by rotating the dry cubes in a cask with a fine dust of pure Paris blue.

Constitution of the Blue Compounds.—It is certain that all forms of blue contain both Fe^{II} and Fe^{III}, since ferrous ferrocyanide is white, and ferric ferricyanide is brown and soluble. Müller and Stanisch (J. pr. Chem. 1909, [ii], **79**, 81) and Müller (Chem.-Ztg. 1914, **38**, 281, 328) calculated from the known normal potentials of the ionic reactions:

$$Fe^{++} \rightleftharpoons Fe^{+++}+\ominus$$

and $$Fe(CN)_6''' + \ominus \rightleftharpoons Fe(CN)_6'''',$$

that the equilibrium constant of the reaction

$$Fe^{+++}+Fe(CN)_6'''' \rightleftharpoons Fe^{++}+Fe(CN)_6''',$$

$$k(=[Fe^{+++}][Fe(CN)_6'''']/Fe^{++}][Fe(CN)_6'''])$$

is approximately 10^{-5}, so that, in a solution containing all these ions, the equilibrium would be practically completely on the side of ferrous ferricyanide. P. Woringer (J. pr. Chem. 1913, [ii], **89**, 51) was indeed able to show that ferricyanide is formed when ferric chloride reacts with an excess of ferrocyanide, and concluded that a ferricyanide structure must be assigned to the blue compounds. It is not permissible, however, to deduce from solution equilibria the composition of a precipitate, which is controlled by solubility relationships. If, for example, the ratio of the solubility products of ferric ferrocyanide ($[\mathrm{Fe}^{+++}][\mathrm{Fe(CN)}_6'''']$) and ferrous ferricyanide ($[\mathrm{Fe}^{++}][\mathrm{Fe(CN)}_6''']$) is less than $k(=10^{-5})$, then practically complete precipitation of ferric ferrocyanide could occur from a solution containing ferrous and ferricyanide ions, in spite of the fact that the ionic equilibrium is entirely in favour of the alternative compound.

It follows that only one of the two alternative compounds is stable, that mixtures of the two cannot exist in contact with solution, and that the composition of an equilibrium product must always be either ferrous ferricyanide or ferric ferrocyanide, independent of the starting materials. The ratio of the two solubility products is unknown, for neither has been measured. On the basis of the Abegg-Bodländer theory of electro-affinity, however, we may predict that the solubility of the compounds formed from the more highly charged ions Fe^{+++} and $\mathrm{Fe(CN)}_6''''$ of weaker electro-affinity will be considerably lower than that of the compounds from the ions $\mathrm{Fe}^{++}$and $\mathrm{Fe(CN)}_6'''$, of lower electrovalency and stronger electro-affinity, so that the blue compounds are probably ferrocyanides.

The chemical evidence must be interpreted with caution. The conclusions of Hofmann and his collaborators (Annalen, 1904, **337**, 1; 1907, **352**, 54) that insoluble Prussian blue is ferric ferrocyanide, because it is formed from ferric ferricyanide and hydrogen peroxide, which reduces ferricyanide and not ferric ion, and of Eibner and Gerstacker (Chem.-Ztg. 1913, **37**, 137, 138, 195) that the blue compound made by the sulphite-reduction of ferric ferricyanide is ferrous ferricyanide, because sulphite reduces only ferric ion, are unsound because the alternative products might be formed from the original reduction products in each case by the operation of Müller's equilibrium. The best reason for regarding insoluble Prussian blue as ferric ferrocyanide is that it is not oxidised by oxygen or by hydrogen peroxide, so that its divalent iron is in the complex: its method of formation from ferric salt and soluble Prussian blue suggests that the soluble blue is also a ferrocyanide: and since Turnbull's blue is produced from soluble Prussian blue and ferrous salt, it must also be a ferrocyanide.

The conception of Prussian and other blues as simple iron ferrocyanides is not entirely satisfactory, however, because it leaves unexplained their differing degrees of stability towards alkalis and oxidising agents, and does not account for their remarkably deep colours, which would not be expected of compounds formed by the simple combination of feebly-coloured ions (Hantzsch, Z. physikal. Chem. 1910, **72**, 362). Reihlen and Zimmermann (Annalen, 1927, **451**, 75; 1929, **475**, 101) and Reihlen and von Kummer (Annalen, 1929, **469**, 30) have put forward the view that the iron cyanide complex in the blue compounds contains both $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$, with which CN is co-ordinated. They apply the same principle to other insoluble ferrocyanides such as the cupric and zinc salts, the $\mathrm{Fe^{III}}$ in the blue complex being replaced in these cases by $\mathrm{Cu^{II}}$ and $\mathrm{Zn^{II}}$ respectively, and to double salts of ferrocyanide, such as Everitt's salt, $\mathrm{K_2Fe[Fe^{II}(CN)_6]}$, which they write as $\mathrm{K_2[Fe^{II}{}_2(CN)_6]}$. This method of formulation simplifies considerably the constitutional problems of the iron cyanogen blue compounds. Only two alkali-free compounds are possible: (*a*) $\mathrm{Fe^{III}[Fe^{II}Fe^{III}(CN)_6]_3}$, in which one-seventh of the total iron is reducible by sulphite, and which is readily identified with insoluble Prussian blue, and (*b*) $\mathrm{Fe^{II}[Fe^{II}Fe^{III}(CN)_6]_2}$, in which one-fifth of the total iron is oxidisable by hydrogen peroxide, and which is Turnbull's blue; and soluble Prussian blue is the potassium salt of the ferro-ferri-complex

$$\mathrm{K[Fe^{II}Fe^{III}(CN)_6]}.$$

The interconversions of soluble and insoluble Prussian blues and Turnbull's blue are readily explained. Cambi and Clerici (Gazzetta, 1928, **58**, 57) accept the theory of the complex containing both divalent and trivalent metals co-ordinated with cyanide for all coloured complex cyanides; for example, the bluish-green ferrous manganicyanide, usually written

$$\mathrm{Fe_3{}^{II}[Mn^{III}(CN)_6]_2},$$

is decomposed by alkali into manganic hydroxide, $\mathrm{Mn(OH)_3}$, and ferrocyanide, whereas the colourless ferrous cobalticyanide $\mathrm{Fe_3{}^{II}[Co^{III}(CN)_6]_2}$, gives ferrous hydroxide, $\mathrm{Fe(OH)_2}$, and cobalticyanide. Hence the colourless cobalt compound is correctly formulated above, but the coloured manganese compound should be written $\mathrm{Mn^{III}[Fe^{II}Mn^{II}(CN)_6]_3}$, or as a similar more complex derivative.

Potassium ferrocyanide, "yellow prussiate of potash," $\mathrm{K_4Fe(CN)_6,3H_2O}$, crystallises from aqueous solutions in large, monoclinic tetragonal pyramids of sp.gr. 1·86. The crystals are stable in air at the ordinary temperature, but begin to lose water at 60°C., being completely dehydrated at 100°C. to give a white powder. On further heating in the absence of oxygen, the powder decomposes, first into Williamson's salt, $\mathrm{K_2Fe[Fe(CN)_6]}$, without gas formation, and then below red heat into a mixture of potassium cyanide, carbon and iron, with nitrogen escaping. According to Hackspill and Pinck (Bull. Soc. chim. 1931, [iv], **49**, 54) considerable quantities of cyanogen are obtained at 300–400°C. The salt is soluble in water, giving the following saturated solutions (Farrow, J.C.S. 1926, **129**, 49); the solubilities are expressed as grams of anhydrous salt in 100 g. of solution:

Temp. °C.	24·9	34·9	49·8
Solubility	23·95	28·01	33·13
Density	1·173	1·202	1·235
Temp. °C.	64·7	79·6	99·7
Solubility	36·94	40·45	43·78
Density	1·264	1·285	1·312

It is insoluble in alcohol.

Potassium and other ferrocyanides are completely decomposed by boiling with mercuric oxide, giving the undissociated mercuric cyanide, ferrous hydroxide and potassium hydroxide. They are also decomposed by aurous cyanide or hydroxide, or by finely divided gold in the presence of oxygen, the complex aurocyanide being formed, as in the cyanide process for dissolving gold (*see under* Gold Cyanides, p. 486), together with ferric hydroxide (Beutel, Z. anorg. Chem. 1912, **78**, 141).

Sodium ferrocyanide,

$$Na_4Fe(CN)_6,10H_2O,$$

crystallises in large lemon-yellow monoclinic prisms or rhombohedra, stable in air at the ordinary temperature, but completely dehydrated at about 100°C. The dry salt decomposes like the potassium salt on strong heating. The concentrations and densities of saturated solutions have been measured by Farrow (J.C.S. 1926, **129**, 49); solubilities are expressed in grams of anhydrous salt per 100 g. of solution:

Temp. °C.	24·9	34·9	49·8
Solubility	17·11	20·58	26·20
Density	1·131	1·158	1·200
Temp. °C.	64·7	79·6	84·7
Solubility	31·43	36·85	38·15
Density	1·243	1·279	1·292
Temp. °C.	89·6	94·7	99·7
Solubility	38·08	38·25	37·53
Density	1·296	1·287	1·286

A transition point to a lower hydrate occurs at 81·7°C.

Zinc ferrocyanide, $Zn_2Fe(CN)_6,6H_2O$, is a white amorphous precipitate obtained by the action of calcium or hydrogen ferrocyanide on excess of zinc chloride in aqueous solution. When other soluble ferrocyanides are used, the precipitate contains varying amounts of the other metal (*see* Treadwell and Chervet, Helv. Chim. Acta, 1923, **6**, 559). Reihlen and Zimmermann (Annalen, 1927, **451**, 75) postulate the existence of complex anions containing both zinc and iron, analogous to the copper ferrocyanides and to the Prussian blues. Zinc ferrocyanide is insoluble in dilute acids, completely soluble in alkalis with formation of ferrocyanide and zincate, but only partially decomposed by alkali carbonates.

Hexamethylcarbylamine ferro-salts.—By the action of methyl sulphate on dry potassium ferrocyanide, or of methyl iodide on silver ferrocyanide, E. G. J. Hartley (J.C.S. 1910, **97**, 1066, 1725; 1911, **99**, 1549; 1912, **101**, 705; 1913, **103**, 1196) has obtained a series of salts of the general formula $[Fe(CNCH_3)_6]R_2$, R being a univalent acid radicle and the iron cyanogen complex acting as a kation. On heating with concentrated sulphuric acid, or on boiling with aqueous caustic soda, they are decomposed with quantitative production of methylamine or methylcarbylamine, showing that all the nitrogen atoms are linked to methyl groups.

Tetramethyl ferrocyanide,

$$\left[Fe\begin{matrix}(CNCH_3)_4\\(CN)_2\end{matrix}\right]$$

is formed when hexamethylcarbylamine ferrochloride, $[Fe(CNCH_3)_6]Cl_2$, a representative of the above class of compounds, is heated at 140–150°C. *in vacuo* for 6–9 hours, when methyl chloride is split off. Hexamethylcarbylamine ferrochloride itself is produced when

$$[Fe(CNCH_3)_6][CH_3SO_4]_2,$$

the initial product of the interaction of potassium ferrocyanide with dimethyl sulphate, is boiled with hydrochloric acid or barium chloride. There are two isomeric forms of tetramethyl ferrocyanide, both of which are present in the above product. The α-isomer is much more soluble in water and organic solvents than is the β-isomer, and crystallises with 2 molecules of water of crystallisation, against 6 in the case of the β-isomer. The α-isomer does not dissociate electrolytically in solution, but the β-isomer (according to Hölzl, *et al.*, Monatsh. 1927, **48**, 71) is an electrolyte. The α-compound combines with methyl iodide at 100°C. to give hexamethylcarbylamine ferroiodide, but the β-compound has no reaction. No method of converting one form into the other has been discovered.

Ferricyanides.

Technical Methods of Preparation. 1. *By Chemical Oxidation of Ferrocyanides.*—The commonest oxidising agent is gaseous chlorine, which may react either with solid potassium ferrocyanide, in which case the product is a solid containing potassium chloride, or with a cold 10% solution of ferrocyanide:

$$2K_4Fe(CN)_6+Cl_2=2K_3Fe(CN)_6+2KCl$$

The reaction is stopped when the conversion of the ferrocyanide is just completed, for excess of chlorine destroys the complex radicle. In practice, a small amount of Prussian green is always formed, which spoils the appearance of the product. The difficulty may be avoided by evaporating the solution to the crystallising point and then adding caustic potash to decompose the Prussian green into ferric hydroxide, which can be filtered off, and potassium ferrocyanide, which is apt to contaminate the crystallised ferricyanide. A yield of 85–90% is obtained in the process.

In order to overcome the above objections to the use of chlorine, lead peroxide, calcium plumbate and potassium permanganate have been suggested as alternative oxidising agents, but have achieved no technical importance (Aten, Chem. Weekblad, 1921, **18**, 140). More recently, the use of air containing carbon dioxide at a pressure of 80 to 120 atmospheres and a temperature of 80° to 100°C. has been proposed (Gluud and Keller, U.S.P. 1872929, 1932) for oxidising potassium ferrocyanide solution. W. Klempt (U.S.P. 1908516, 1933) describes a similar process for calcium ferrocyanide solution.

2. *By Electrolytic Oxidation of Ferrocyanides.*—The electrolysis of ferrocyanide solutions gives rise to ferricyanide and alkali at the anode:

$$Fe(CN)_6''''=Fe(CN)_6'''+\ominus;$$
$$H_2O+\ominus=OH'+\tfrac{1}{2}H_2$$

This method of converting ferrocyanide into ferricyanide has been investigated by Grube from the electrochemical standpoint (Z. anorg. Chem. 1914, **84,** 190; Z. Elektrochem. 1914, **20,** 334). In practice, the electrolysis of neutral ferrocyanide solutions is carried out at 60°C. in diaphragm cells with nickel electrodes. Potassium ferricyanide crystallises out from the anode liquor on cooling, and the mother liquor is replenished with ferrocyanide and returned to the cell. The purpose of using a diaphragm is to prevent reduction of ferricyanide at the kathode, with consequent decrease of current efficiency. According to Paweck and Hirsch (Z. Elektrochem. 1928, **34,** 684), the diaphragm can be omitted if an alternating current is superimposed on the direct current.

PROPERTIES OF THE FERRICYANIDES.—**Potassium ferricyanide,** "red prussiate of potash," $K_3Fe(CN)_6$, is prepared in the laboratory by the electrolytic oxidation of an alkaline solution of potassium ferrocyanide, or by the technical method of oxidation with chlorine. The salt crystallises anhydrous from water in magnificent, deep red, monoclinic prisms, of density 1·858 (Biltz). The crystals are isomorphous with the cobalti-, mangani-, and chromicyanides of potassium. The salt is decomposed by 20% sulphuric acid on heating to yield hydrocyanic acid, and with 80% acid it gives carbon monoxide and carbon dioxide (Bassett and Corbet, J.C.S. 1924, **125,** 1358).

The properties of saturated solutions have been measured by Friend and Smirles (J.C.S. 1928, 2242); the solubilities are expressed in grams of salt per 100 g. of solution:

Temp. °C.	0·1	7·8	15·7
Solubility	23·22	26·96	30·35
Density	—	1·157	1·174
Temp. °C.	22·1	26·3	39·9
Solubility	32·08	33·66	37·22
Density	1·187	1·193	1·212
Temp. °C.	58	81	99
Solubility	41·10	44·70	47·60
Density	1·227	—	—

The aqueous solution is decomposed by light to give ferrocyanide. The solution is not as stable as ferrocyanide solution, for on heating with carbon dioxide at 80–100°C. it is appreciably hydrolysed with the formation of pentacyanide. Ferricyanides in caustic potash solution are relatively strong oxidising agents, decolourising indigo instantaneously, and being also reduced by hydrogen peroxide with liberation of oxygen.

Ferric ferricyanide.—When ferricyanide and ferric salt solutions are mixed a reddish-brown colloidal solution is obtained, which is believed to contain ferric ferricyanide. Haller (Kolloid-Z., 1917, **20,** 76) examined the solution ultramicroscopically, and showed that the colloidal particles gradually increase in size and a green substance separates out. Reihlen and von Kummer (Annalen, 1929, **469,** 30) produced brown, slightly soluble microcrystals of $Fe_2(CN)_6,2H_2O$ from acid solutions of potassium ferricyanide and ferric nitrate. Green ferric ferricyanides are obtained by boiling Prussian blue with concentrated nitric acid, or from potassium ferricyanide and ferric chloride.

Pentacyanides.

As already mentioned (p. 466), the iron hexacyanides can undergo a decomposition of the complex by which one ionic cyanide group is replaced by a molecular group, giving a new pentacyanide complex with a valency lower than that of the original complex. The most important transformations of hexacyanides into pentacyanides are listed in the table below.

Other substituents which may be found in complex pentacyanides are NO_2, AsO_2, SO_3, NH_3, and substituted ammonias.

The correct constitution of the nitroprussides was first given by Gerhardt (Traité de chimie organique, 1853, I, 344). K. A. Hofmann carried out extensive work on their reactions (Z. anorg. Chem. 1895, **10,** 262; 1896, **11,** 31, 278; 1896, **12,** 146), and was able to explain his observations on the basis of the co-ordination theory (Hofmann, Annalen, 1900, **312,** 1). Other important work on the transition of hexacyanides into pentacyanides is described by Manchot (Ber. 1912, **45,** 2869), Cambi (Gazzetta, 1911, [i], **41,** 157) and Jimori (Z. anorg. Chem. 1927, **167,** 145).

	Ferrocyanide $[Fe(CN)_6]''''$ gives	Ferricyanide $[Fe(CN)_6]'''$ gives
By warming aqueous solutions, action of light or acids By action of strong oxidising agents on solutions	aquopentacyanoferroate, $[Fe(CN)_5H_2O]'''$	aquopentacyanoferriate, $[Fe(CN)_5H_2O]''$
By heating solutions with carbon monoxide	carbonylferrocyanide, $[Fe(CN)_5CO]'''$	carbonylferrocyanide, $[Fe(CN)_5CO]'''$
By warming with nitric or nitrous acid	nitrosoprussiate, $[Fe(CN)_5NO]''$ (nitroprusside)	nitrosoprussiate, $[Fe(CN)_5NO]''$ (nitroprusside)

Potassium carbonylferrocyanide,

$$K_3[Fe(CN)_5CO]H_2O,$$

is formed by the action of carbon monoxide on an aqueous solution of potassium ferrocyanide at 135°C. in a sealed tube (Müller, Ann. chim. phys. 1889, [vi], **17,** 94):

$$K_4Fe(CN)_6+CO+2H_2O = K_3[Fe(CN)_5CO]+NH_3+HCOOK$$

It may also be made by heating potassium ferrocyanide with sulphuric acid until the evolution of carbon monoxide begins, and then cooling (*see* Hölzl, Monatsh. 1930, **56**, 79). Carbonylferrocyanides are present in the cyanide mud and spent oxide of the purification plant of gas works; according to Colman (Analyst, 1908, **33**, 261), from 2 to 5% of the cyanogen (and sometimes as much as 20%) is present in this form. When cyanide mud and spent oxide are extracted with caustic soda, and the extract mixed with 5 times its volume of methylated spirit, the sodium ferrocyanide crystallises out completely in a few hours, after which the carbonylferrocyanide can be precipitated as the amorphous, deep violet ferric salt by adding ferric chloride to the acidified solution. The deliquescent calcium salt, which crystallises with 8 molecules of water, is obtained by boiling the ferric salt with milk of lime. The copper salt, a green precipitate soluble in excess of ammonia, is characteristic. The carbonylferrocyanides resemble the corresponding ferrocyanides, but are paler in colour, more soluble in water, and more stable towards oxidising agents.

Sodium nitroprusside,

$$Na_2[Fe(CN)_5NO]2H_2O,$$

is made by the action of dilute nitric acid on a ferrocyanide solution (Playfair, Phil. Mag. 1850 [3], **36**, 197). The solution is neutralised with sodium carbonate and evaporated to crystallise out potassium nitrate, which is separated before finally crystallising the nitroprusside. The mechanism of its formation is that the nitric acid oxidises the ferrocyanide to ferricyanide, itself being reduced to nitric oxide, and the two products then react in accordance with the equation:

$$Fe(CN)_6'''+NO+H^+ = [Fe(CN)_5NO]''+HCN$$

The salt can also be formed from solutions of ferrous sulphate, sodium nitrite and potassium cyanide. It crystallises in dark red prisms, soluble in $2\frac{1}{2}$ parts of water at 16°C. The solution is not precipitated by a ferric salt, and gives a deep violet coloration with alkali sulphides.

Sodium aquopentacyanoferroate,

$$Na_3[Fe(CN)_5H_2O]5H_2O,$$

is obtained by the action of reducing agents such as phenylhydrazine or hydroxylamine, or of oxidising agents such as potassium hypobromite or hydrogen peroxide, on sodium nitroprusside solution below 0°C. The **NO** group of the nitroprusside is replaced by water, and the iron of the complex is converted from Fe^{III} to Fe^{II}. In the latter respect, the action of hydrogen peroxide is analogous to its behaviour with ferricyanide, which it reduces to ferrocyanide. The salt crystallises in reddish-yellow needles, giving an intensely yellow solution which does not yield a violet coloration with alkali sulphides.

Sodium aquopentacyanoferriate,

$$Na_2[Fe(CN)_5H_2O],$$

is obtained by oxidising the ferroate compound (described above) with bromine water. It is a deep violet-blue substance. The corresponding potassium salt is obtained by the action of excess chlorine on potassium ferricyanide, and is identical, according to Cambi (Gazzetta, 1911, **41**, I, 57), with the "potassium perferricyanide" obtained by Bong (Bull. Soc. chim. 1875, [ii], **24**, 268) and Skraup (Annalen, 1877, **189**, 368) by the action of potassium chlorate on potassium ferricyanide solution.

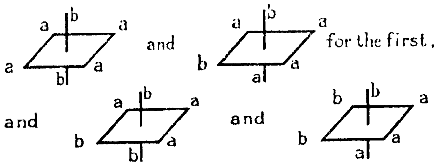
Constitution of the Complex Iron Cyanides.—According to Werner's co-ordination theory ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 5th ed., 1923), complex salts are to be regarded as built up by the "co-ordination," through co-valent, non-ionisable linkages, of a number of atomic groups round a central atom, giving a more or less stable nucleus. According to the nature of its component parts this nucleus may or may not be able to combine with other atoms by means of electrovalent, ionisable links. The significance of the square brackets in the usual method of writing Wernerian formulæ is that all the linkages between groups within the brackets are non-ionisable. The co-ordination number of the central atom bears no obvious relation to its valency; the maximum co-ordination number of carbon, nitrogen and boron is 4, of the great majority of elements is 6, and of some of the heavier elements (*e.g.* molybdenum and tungsten) is 8.

The great stability of the ferrocyanides and ferricyanides has already been mentioned. The first decomposition of the complex ions is the removal of one cyanogen ion, which is always replaced by another molecular group, such as H_2O, NO, or CO, giving a new complex in which the iron atom is still associated with six groups. Thus the whole series of complex iron cyanides, derived from divalent and tri-valent iron, provides an example of co-ordinated compounds in which the iron (in either valency state) has a well-defined co-ordination number of 6. The following list of compounds illustrates the way in which the electrovalency of the 6-co-ordinated complex is altered by the abstraction of one or more cyanide ions, to be replaced by the same number of neutral atomic groups:

Ferro series.		Ferri series.		Complex form.
$[Fe^{II}(CN)_6]''''$	$4K^+$	$[Fe^{III}(CN)_6]'''$	$3K^+$	anion
$\left[Fe\begin{matrix}(CN)_5\\CO\end{matrix}\right]'''$	$3K^+$	$\left[Fe\begin{matrix}(CN)_5\\CO\end{matrix}\right]''$	$2K^+$	anion
$\left[Fe\begin{matrix}(CNCH_3)_4\\(CN)_2\end{matrix}\right]^0$		$^*\left[Co\begin{matrix}(CNCH_3)_3\\(CN)_3\end{matrix}\right]^0$		not ionised
$[Fe(CNCH_3)_6]^{++}$	$2Cl'$			kation

* The corresponding ferricyanide derivative is wanting (Hartley, J.C.S. 1914, **105**, 521).

In the case of a complex containing six co-ordinated groups, Werner held that the six groups are arranged symmetrically at the corners of a regular octahedron, the co-ordinating atom being at the centre. Hence complexes of the general formulæ Ma_4b_2 and Ma_3b_3 should exist in the two stereoisomeric forms represented by:



for the second. Hartley's two isomeric tetramethyl ferrocyanides (p. 475) are regarded as stereoisomers by Glasstone (J.C.S. 1930, 321), and the same may be true of his isomeric trimethyl cobalticyanides (*ibid.* 1914, **105**, 521).

On the other hand, no isomerism would be expected in the simple ferro- and ferri-cyanides. Briggs (*ibid.* 1911, **99**, 1019) described α- and β-isomers of alkali ferrocyanides with slight differences in physical properties, but Bennett (*ibid.* 1917, **111**, 490) showed that the two forms are crystallographically identical, and Piutti (Ber. 1912, **45**, 1830) and Getman (J. Physical Chem. 1921, **25**, 147) found no differences in the absorption spectra. Locke and Edwards (J. Amer. Chem. Soc. 1899, **21**, 193, 413) described the conversion of ordinary red α-potassium ferricyanide into an isomeric green β-modification by treatment with acids. The green product had a different crystalline form, absorption spectrum (Getman, *l.c.*), and chemical properties (Bellucci and Sabatini, Atti R. Accad. Lincei, 1911, [V], **20**, I, 176). The view is now held by Briggs (J.C.S. 1920, **117**, 1026; J. Physical Chem. 1928, **32**, 1422) that no isomerism exists in the alkali ferro- and ferri-cyanides, the observed differences in the properties of the β-forms being due, in the case of ferrocyanide, to the presence of small amounts of aquopentacyanoferroate, $K_3[Fe(CN)_5H_2O]$, and in the case of ferricyanide, to the existence of a double salt between ferricyanide and aquopentacyanoferriate having the formula

$$3K_3[Fe(CN)_6]\cdot K_2[Fe(CN)_5H_2O].$$

It is a shortcoming of Werner's theory that his structural formulæ lack the definiteness of those of organic chemistry, and that the existence is implied of a new kind of valency for the co-ordinating atom, having no relation to its normal electrovalency or covalency. The difficulty has been dispelled by the application of the electronic mechanism of valency to co-ordination (Sidgwick, J.C.S. 1923, **123**, 725; "The Electronic Theory of Valency," 1927). According to the electronic interpretation, a covalent, non-ionisable linkage is formed by the sharing of two electrons between the combining atoms, each electron simultaneously forming a part of the stable electron configurations of both atoms. In the normal covalent link, one shared electron is provided by each of the atoms, but in the co-ordinated link both are supplied by one of the atoms, termed the "donor." Hence a co-ordination number of 4 corresponds to the formation of a stable octet of electrons, and of 6 to the formation of a ring of twelve, another stable configuration.

While the concept of 6-co-ordinated iron gives a satisfactory representation of the properties of the simple ferro- and ferri-cyanides of the alkali and alkaline earth metals, difficulties arise in the case of the heavy metal salts such as Prussian blue, copper ferrocyanide, and zinc ferrocyanide, which have been met by the assumption of a complex having two nuclear atoms, *e.g.* Fe^{II} and Fe^{III} in the case of Prussian blue (*see under* Constitution of the Blue Compounds, p. 473), Zn and Fe^{II} in the case of zinc ferrocyanide. In these cases the co-ordination number of each of the nuclear metallic atoms is probably 4. Similar bi-nuclear complexes may exist in the numerous double salts formed by ferrocyanides, the less electropositive of the two metals tending to enter the ferrocyanide complex. In this connection it is of interest to note that Berkeley, Hartley and Stephenson (Phil. Trans. 1909, **209**,A, 319) conclude, from measurements of the osmotic pressure and electrical conductivity of solutions of ferrocyanides of calcium and strontium, that these salts give in solution undissociated molecules of twice the simple formula-weights, indicating a tendency to similar binuclear complex formation even in the alkaline earth ferrocyanides.

II. ALKALI METAL CYANIDES.

TECHNICAL METHODS OF PREPARATION.—1. *From Ferrocyanides.* The earliest method of preparing potassium cyanide from ferrocyanide, due to Berzelius, consisted in heating dry potassium ferrocyanide to redness:

$$K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$$

A 33% loss of cyanogen occurs in this reaction, which can be reduced by adding potassium carbonate so that the fusion is carried out with a mixture of 8 parts of ferrocyanide to 3 parts of potash (F. and E. Rodgers, Phil. Mag. 1834, [3], **4**, 91). The melt is allowed to stand until the iron and carbon have separated out, and is then poured into moulds, giving white, porcelain-like cakes containing from 30 to 70% of **KCN**. This product was used until about 1890 for electroplating and other purposes. Liebig showed that cyanate was formed during the reaction, thus:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2$$

Fleck ("Die Fabrikation chemischer Produkte aus tierischen Abfällen," 1862) and Chaster (B.P. 15941 of 1894) proposed the use of charcoal to reduce the cyanate, but it appears unlikely that this reduction would occur at the relatively low temperatures used in the fusion.

Erlenmeyer (Ber. 1876, **9**, 1840) described a much more advantageous process, in which a pure product containing approximately 40% **CN** (equivalent to 100% **KCN**) was obtained by fusing dry potassium ferrocyanide with metallic sodium in the proportions required by the equation:

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$$

The process became technically important in the hands of the Deuts. Gold-u.-Silber-Scheideanstalt vorm. Roessler, V. Intern. Kongress für Angewandte Chemie, Berlin, 1903, I, 638) when sodium became a commercial product in 1890. The spongy iron is filtered off from the melt and then pressed out while still red-hot; the filtered cyanide is cast in cakes and gives a very pure commercial product. Since 1905, sodium ferrocyanide has been used instead of the potassium salt, and the product is almost pure sodium cyanide. In England the surplus of ferrocyanide from gas works over that required in the colour industries was formerly converted into cyanide by this process. Modifications have been described by Hetherington, Muspratt and Hurter (B.P. 5832 of 1894), who used a sodium-lead alloy instead of sodium and obtained a three-layer product, the powdered iron floating between the upper liquid cyanide and the lower liquid lead, and by Crowther and Rossiter (B.P. 9275 of 1894), who used zinc alone for reducing the ferrocyanide, subsequently decomposing the zinc cyanide by fusion with alkali carbonate. Neither modification has achieved practical importance.

2. *From Ammonia and Alkali Carbonates.*—Two important processes which have been large producers of cyanide, utilising the same reactions but under considerably different working conditions, fall under this head. In Siepermann's process (G.P. 38012 of 1886; B.P. 13697 of 1889, 9350 and 9351 of 1900) a dry mixture of 2 parts of wood charcoal and 1 part of potassium carbonate is introduced into the upper end of a vertical iron retort, and is treated at a dull red heat with dry ammonia gas introduced at a point about half-way down the length of the retort. Absorption of the ammonia occurs with production of potassium cyanate, probably through the intermediate formation of potassium carbamate (according to Pfleger, *see* Deuts. Gold-u.-Silber-Scheideanstalt vorm. Roessler, V. Intern. Kongress für Angewandte Chemie, Berlin, 1903, I, 638):

$$CO(OK)_2+NH_3=CO(NH_2)OK+KOH$$

$$CO(NH_2)OK=KCNO+H_2O$$

The product then falls into the lower part of the retort, which is maintained at a bright red heat. At the higher temperature the cyanate is converted into cyanide, and carbon monoxide is produced which escapes through the upper part of the retort with the hydrogen formed by the decomposition of some of the ammonia. According to Pfleger (*l.c.*) the conversion of the cyanate proceeds in two stages :

$$2KCNO=K_2CN_2+CO_2$$

(*cf.* Drechsel, J. pr. Chem. 1877, [ii], **16**, 201, on a similar decomposition of alkaline earth cyanates), and

$$K_2CN_2+C=2KCN$$

Drechsel, J. pr. Chem. 1880, [ii], **21**, 77) ;finally:

$$CO_2+C=2CO.$$

Some of the potassium cyanamide may decompose directly into cyanide, potassium and nitrogen, as this reaction is known to occur below 800°C. in the absence of excess charcoal. The product of Siepermann's process is allowed to cool out of contact with air, and is then systematically leached with exclusion of air (B.P. 9351 of 1900). Potassium cyanide may be precipitated from the extract by adding excess of potassium carbonate, or better by evaporating nearly to dryness and extracting unchanged potassium carbonate with a minimum quantity of water at 66°C. The residue, containing potassium cyanide and some unconverted cyanate, is treated with refrigerated water (between −18° and +5°C.) to dissolve the cyanide and leave the cyanate, and the cyanide is crystallised as a damp, deliquescent mass (B.P. 9352 of 1900). This product had to be fused with cyanide produced from ferrocyanide in order to make it suitable for export to the gold mines.

The second process of this kind is the Beilby process (B.P. 4820 of 1891), which first became a producer in 1892, the same year as Siepermann's. Gaseous ammonia is forced through molten potassium carbonate, and the addition of charcoal is made gradually, the total quantity added being hardly more than that theoretically required by the equation :

$$K_2CO_3+4C+2NH_3=2KCN+3CO+3H_2$$

In this way the leaching step of Siepermann's method is avoided, for it is possible to run off the molten mass from the retorts, through filters for the small amount of unreacted charcoal, directly into moulds to give a white, saleable product. In practice, previously made cyanide was added to the potassium carbonate on starting the process, in order to lower the melting-point of the reaction mass, and the passage of ammonia was continued until an analysis of the melt showed that the reaction was complete. The reaction temperature was 900–1000°C., and the formation of cyanate and its conversion into cyanide occur simultaneously.

As regards the relative merits of the two processes, Siepermann's gives higher yields of cyanide based on the ammonia used because, at the lower temperature of the first stage reaction, less decomposition of ammonia into its elements occurs. The higher temperature in Beilby's process is necessary, however, for the maintenance of a reasonably high rate of reaction since by working in a medium of molten salt the advantage of the large surface exposed by Siepermann's dry mass of alkalised charcoal is sacrificed. The dissociation of the ammonia in Beilby's process is minimised by introducing the gas into the retort through tubes lined with copper, this metal having no catalytic effect on the decomposition of ammonia. The yields on ammonia actually obtained are 80–85% in Siepermann's, and 55–60% in Beilby's process. According to Readman (J.S.C.I. 1889, **8**, 757) it is possible to obtain an almost quantitative yield by working at a low enough temperature. The great advantage of Beilby's process is the easy working-up of the product into a readily marketable form.

3. *From Ammonia and Alkali Metals.*—The reaction of sodium with charcoal and ammonia to give sodium cyanide was proposed by Castner in 1894 (B.P. 12219 of 1894; G.P. 90999, F.P.

239643), and rapidly became the most important process in use for cyanide manufacture. The complete reaction is represented by the equation:

$$2Na+2C+2NH_3=2NaCN+3H_2$$

According to Castner's earlier claims (B.P. 21732 of 1894), the reaction is best carried out in two stages, in the first of which liquid sodium is allowed to react with dry ammonia gas at 300–400°C. in a horizontal cast iron retort fitted with a series of vertical baffles to increase the length of passage of the gas over the liquid. Sodamide is formed, which is stable up to temperatures approaching 500°C. (Titherley, J.C.S. 1894, **65**, 504):

$$2Na+2NH_3=2NaNH_2+H_2$$

In the second stage the molten sodamide is run on to red-hot wood charcoal in a vertical cylindrical retort. Carbon absorption occurs with the formation of sodium cyanamide, a compound which is relatively stable up to 600°C.:

$$2NaNH_2+C=Na_2CN_2+2H_2$$

Cyanamide may also be formed, according to Pfleger, by the interaction of sodamide and sodium cyanide already formed:

$$NaNH_2+NaCN=Na_2CN_2+H_2$$

The second stage of the Castner process is completed by raising the temperature of the cyanising furnace to 700–800°C., when the cyanamide melt absorbs further quantities of carbon to form molten cyanide:

$$Na_2CN_2+C=2NaCN$$

According to G.P. 148046 (Deuts. Gold-u.-Silber-Scheideanstalt vorm. Roessler), it is possible to carry out the whole process in one retort, the sodamide being produced at the lowest possible temperature, and the temperature then gradually raised for the succeeding stages of the reaction. The molten charge is run off from the retort through filters to remove small amounts of solid impurities (such as unreacted charcoal), and is cast in iron moulds to give pure white cakes with a crystalline fracture, and analysing 97–98% $NaCN$, 2·1% Na_2CO_3, 0·3% $NaCNO$, and 0·02% Na_2S.

Instead of charcoal, volatile organic compounds such as acetylene (G.P. 149678) or trimethylamine (G.P. 223027) may be added to the melt as sources of carbon, but such variations have not come into general practice. The source of the ammonia used in the operation of the Castner process was formerly the by-product of coal distillation, but since 1918 there has been a considerable change-over to the use of synthetic ammonia. This is reflected in H. Freudenberg's B.P. 265639, 1926, which claims the collection and recombination with nitrogen of the hydrogen produced in the Castner cyanide synthesis. This hydrogen is relatively pure, containing only small quantities of methane and nitrogen.

The Castner process was first put into operation at Frankfurt-on-Main in 1899, a second plant was started at Glasgow in 1900, and a third near New York in 1901. Since that time it has continued to provide the greater part of the world's cyanide requirements, and still retains its pre-eminent position.

4. *From Thiocyanates.*—The usual method of preparing cyanides from thiocyanates is first to convert the thiocyanate into ferrocyanide by one of the methods already described (p. 469), and then to work up the ferrocyanide into cyanide by the Erlenmeyer method as described on p. 478. On the other hand, the direct desulphurisation of thiocyanates can be carried out by fusion with lead or zinc (Warren, Chem. News, 1890, **62**, 252; Playfair, B.P. 7764 of 1890). The fusion is carried out at 400°C., and gives a 70–80% conversion to cyanide (Playfair, J.S.C.I. 1892, **11**, 14; Conroy, *ibid.* 1896, **15**, 8), which is extracted from the cooled melt with water. Playfair (*l.c.*) also found that hydrogen reduces potassium thiocyanate at a dull red heat, giving potassium cyanide, potassium sulphide, and sulphuretted hydrogen. Conroy, Heslop, and Shores (J.S.C.I. 1901, **20**, 320) found that, on reduction with hydrogen, about 70% of the nitrogen is obtained as potassium cyanide and 20% is further reduced to hydrocyanic acid. An interesting proposal for the direct desulphurisation of ammonium thiocyanate by heating it with finely divided copper at 300–500°C. has recently been made by König and Siegle and Co. (B.P. 438358 and 438402, 1934). Cuprous sulphide is formed and the vapours of ammonium cyanide are evolved and are absorbed in water to give a dilute solution. It is not possible to separate solid ammonium cyanide from this solution, which is highly unstable on keeping, but it is claimed that the solution is suitable for use in the extraction of gold from its ores.

Zinc oxide may be used as a desulphurising agent if carbon monoxide is also present. According to G.P. 588823, 1932 (N.V. Stikstofbindingsindustrie, Nederland), a 96% yield of sodium cyanide is obtained by heating sodium thiocyanate above 400°C. with zinc oxide and a gas containing carbon monoxide:

$$NaCNS+ZnO+CO=NaCN+ZnS+CO_2$$

Lime or chalk may be used instead of zinc oxide (B.P. 401627, 1932); in this case the initial crude product contains a high percentage of sodium cyanate, which can be reduced to cyanide, however, by continuing the passage of carbon monoxide:

$$NaCNS+CaO=NaCNO+CaS$$
$$NaCNO+CO=NaCN+CO_2$$

5. *From Hydrocyanic Acid.*—The recovery of the hydrocyanic acid content of "Schlempe" gases (*see* Hydrocyanic Acid, p. 493), in the form of solid sodium cyanide is an important technical process. The cyanised gas, which contains 7% HCN, 7% NH_3, and 24% CO_2 by volume, is freed from ammonia by scrubbing with dilute sulphuric acid, and separated from carbon dioxide and enriched in hydrocyanic acid by scrubbing with water and fractionally distilling the aqueous HCN-extract. The gas containing the concentrated HCN thus obtained is

absorbed in aqueous caustic soda of such a strength that a saturated solution of sodium cyanide (45% by weight) is produced (Muhlert, Chem. App. 1925, **12**, 156). This solution is evaporated *in vacuo* to a paste, which is centrifuged to give a product containing 10% of water, from which the rest of the water is removed by drying on heated trays *in vacuo*. The dried powder is then briquetted (B.P. 18096 of 1907), and the product appears in commerce with the following analysis: $NaCN$ 92–93%, Na_2CO_3 3·5%, $NaCNO$ 0·7%, $NaCl$ 1·0%, $NaOH$ 0·5%, Na_2SO_4 0·2%, Na_2S 0·02%.

In the above process, prior removal of carbon dioxide from the gas is necessary in order to avoid excessive formation of carbonate during the neutralisation. In carrying out this step, care must be taken that the hydrocyanic acid is not present in excess, because of the tendency of free hydrocyanic acid to polymerise in contact with alkaline substances such as cyanides. If this polymerisation occurs, the product is discoloured and its commercial value impaired. The evaporation of the cyanide solution must be carried out *in vacuo* at a relatively low temperature in order to minimise saponification of the cyanide to formate and ammonia, which results in loss of cyanide efficiency and in formate contamination of the product. Various expedients have been suggested to avoid the evaporation step, but none has found practical application. Interest in the problem has, however, been revived by the development of the newer cyanide syntheses by high-temperature gas reactions and by formamide dehydration, which reactions yield their hydrocyanic acid in the form of a dilute gaseous mixture similar to the cyanised " Schlempe " gas.

According to G.P. 160637, 1903, the gas containing the HCN free from carbon dioxide may be passed over solid flake caustic soda at 200°C., so that the water produced (by the reaction $NaOH+HCN=NaCN+H_2O$) is vaporised, but no melting of the solid occurs. It is necessary in this method to grind the product when it contains 50–60% $NaCN$, in order to expose fresh surfaces of caustic soda to the gas. Wiggers (Z. anal. Chem. 1876, **15**, 448) obtained pure potassium cyanide by reacting hydrocyanic acid with a solution of caustic potash (3 parts) in 95% alcohol (1 part), washing the potassium cyanide precipitate with alcohol and drying it over sulphuric acid. Guignard and Watrigant (G.P. 243469, 1911) used alcoholic caustic soda for the preparation of sodium cyanide, and added metallic sodium from time to time to react with the water produced, so as to prevent the saponification of hydrocyanic acid to ammonia and formic acid.

The evaporation of aqueous cyanide solutions may also be avoided by salting out the cyanide from solution with solid alkali (Tscherniac, G.P. 182774, 1906; Chemische Fabrik Schlempe, G.P. 192884, 1906), the salting liquor being used again in the absorption. The Stassfurt Chemische Fabrik (G.P. 129863, 1901) claims that an anhydrous cyanide containing 43·5% CN can be obtained by crystallising from a solution containing the sodium and potassium salts in the ratio $2KCN{:}NaCN$, whereas sodium cyanide gives the dihydrate.

A considerable amount of work has been done on the interaction of gaseous hydrocyanic acid with solid sodium carbonate to give sodium cyanide:

$$Na_2CO_3+2HCN \rightleftharpoons 2NaCN+H_2O+CO_2$$

In the earlier experiments, high temperatures (700–900°C.) were used, and the cyanide was the run from the reaction chamber in molten state (Roeder and Grünwald, G.P. 134102, 1901. Tscherniac (G.P. 145748, 1902) worked at 450°C., and claimed to produce sodium cyanide of 98–99% quality. More recently attention has been paid to the physical form of the carbonate used, which greatly affects the speed of reaction and the strength of cyanide attainable in the solid product. E. Hene (B.P. 375636, 1931) recommends the use of the light form of sodium carbonate produced by calcining bicarbonate below 500°C., and conducts the absorption of hydrocyanic acid at 360°C. The Gesellschaft für Kohlentechnik (F.P. 751191, 1932) describes the production of similarly reactive carbonate by dehydration of the crystalline hydrates under temperature conditions such that no solution, fusion, or fritting of the salt occurs. The HCN-fixation reaction is reversible, and the equilibrium

$$k=[HCN]^2/[H_2O][CO_2]$$

precludes high percentage conversions of gaseous hydrocyanic acid, unless one or both of the gaseous reaction products, steam and carbon dioxide, are removed from the system. Thus A. D. Macallum (U.S.P. 1966253, 1934) describes the conversion of the hydrocyanic acid in the gaseous product of formamide dehydration (*see* Hydrocyanic acid, p. 495) into solid sodium cyanide by passing the gas over reactive sodium carbonate at 200–500°C., removing either or both of the gaseous by-products, water and carbon dioxide, and re-circulating the residual gas.

6. *From Nitrogen and Alkali Metal Carbonates.*—Of the syntheses of alkali metal cyanides from elementary nitrogen the one which has achieved the greatest practical importance is the action of nitrogen on a mixture of alkali carbonate and carbon, generally in the presence of a metallic catalyst. The reaction is expressed by the equation:

$$Na_2CO_3+4C+N_2=2NaCN+3CO$$

Such a synthesis may have been carried out by Scheele in 1783 (*see* " Chemical Essays," 1901, reprint, p. 288) when he noticed the formation of ferrocyanide on fusing charcoal with alkalis, and was certainly used by L. Thompson (Mechanics Magazine, 1839, **31**, 92) when he substituted atmospheric nitrogen for nitrogenous animal matter in the preparation of ferrocyanides. Thompson realised the importance of the presence of iron, which lowers the temperature necessary for cyanide formation.

The first attempts to carry out the reaction on a technical scale were made by Possoz and

Boissière (B.P. 9985 of 1843) in France, and an *account of further large-scale experiments in England is given by Graham (Report of Juries,* Exhib. of 1851, **1**, 95). Wood charcoal was soaked in a solution of potassium carbonate and dried to give a mixture containing about 20% K_2O, which was heated to a white heat (probably 1,300–1,400°C.) in fire-brick vertical retorts. In order to supply as rapidly as possible the large quantities of heat necessary to attain this high reaction temperature, and to make good the heat absorbed by the endothermic reaction (amounting to 64·5 cals. per g.-mol. of potassium cyanide produced), hot furnace gases (consisting of nitrogen and carbon dioxide) were drawn directly into the cyanising mass through slots in the brickwork of the retort by means of a suction applied at its upper end. Above the high-temperature, cyanising section of the retort was a section in which the preliminary drying of the alkalised charcoal by the hot furnace gases took place; and below it was a cooling section from which the cyanised product was withdrawn into ferrous salt solution for the production of ferrocyanide. The process failed financially owing to high potash losses and the short life of the retorts. About one-third of the alkali and one-half of the charcoal were cyanised.

Victor Alder of Vienna clearly recognised the three important conditions which contribute to the successful operation of this process, namely, the catalytic action of iron (B.P. 1004 of 1880), the intimate admixture of the solid reactants, and the porosity of the charge so as to admit of free access of nitrogen. In B.P. 5617 of 1881 he describes the preparation of the charge by mixing charcoal with alkali and adding sawdust or other material, so that on heating the mixture a porous mass results. The catalytic metal may be added as such, or as oxide, or as a salt solution which will hydrolyse on heating to give a deposit of the oxide, which in turn is reduced to the metal under the cyanising conditions. The catalytic activity of iron (and to a less extent of other metals) was studied by Täuber (Ber. 1899, **32**, 3150; Chem. Ind. 1903, **26**, 26): the average conversion of alkali to cyanide in these experiments was only 10%, and the maximum 25%.

Great progress in this cyanide synthesis was shown by the work of J. E. Bucher in America (Ind. Eng. Chem. 1917, **9**, 233; B.P. 27713 of 1912, 13332 and 23292 of 1914, 2286 of 1915), with the result that the process was commercially developed in that country during the later years of the War of 1914–18. Descriptions of small, semi-technical and full-scale plant appear in the literature, and in addition to the article by Bucher mentioned above, the following may also be consulted: Brown, Ind. Eng. Chem. 1919, **11**, 1010; De Kay Thompson, Chem. Met. Eng. 1922, **26**, 124; Chickering, *ibid.* 1924, **31**, 967). Carbon in the form of charcoal, by-product carbon made by extracting wood charcoal with caustic soda, or coke (which, however, gives inferior results) and iron oxide (Fe_2O_3 or Fe_3O_4) are separately ground to pass a 100-mesh sieve, then reground together and dry sodium carbonate added. The open-grained structure required for easy access of nitrogen is obtained by briquetting the mixture; the powder is kneaded at 100°C. with water sufficient to form the monohydrate Na_2CO_3,H_2O, and the paste extruded in the form of rods 1 in. long and ⅛ in. in diameter, which are dried immediately to prevent decahydrate formation. The proportions of carbon, iron, and sodium carbonate in the mixture are from 2 : 2 : 1 to 2 : 2 : 2, the greatest reaction velocity being obtained with the lowest sodium carbonate content. The reaction temperature is 950–1,000°C., at which the briquettes are slighty plastic: reaction does not occur below 700°C., and temperatures above 1,150°C. (the eutectic of iron-carbon) should be avoided, because fusion of the iron particles diminishes their active surface. The method of heating may be externally by gas or electric power, or internally by using the hot charge itself as an electrical resistance. This last method is preferred by Bucher, since it affords a means of supplying the necessary heat (including that of the endothermic reaction) at a high rate. Pure nitrogen or producer gas may be used as the source of nitrogen. According to De Kay Thompson (*l.c.*), the results with producer gas are inferior, and this may be due to the reversibility of the reaction:

$$\mathrm{Na_2CO_3+4C+N_2} \\ =\mathrm{2NaCN+3CO}-138\cdot5 \text{ k.g.-cals.}$$

The use of producer gas decreases the partial pressure of nitrogen and increases that of carbon monoxide, displacing the equilibrium to the left. De Kay Thompson states that the amount of nitrogen required for satisfactory results is three times the theoretical.

In a typical batch experiment, a carbon-iron-carbonate mixture of the composition 2 : 2 : 1 was heated in 13 minutes from 710° to 920°C. in a current of nitrogen, and gave a product containing 15·2% NaCN, corresponding to a 92% conversion of carbonate into cyanide. At 900–950°C. some volatilisation of sodium cyanide occurs, so that the upper layers of a batch product are richer in cyanide than the lower ones.

The more recent work on this process for cyanide synthesis has been directed towards the development of methods of preparing masses of porous, highly reactive alkalised coke for the reaction. It is claimed that very porous and active briquettes are made by mixing sodium bicarbonate with coke and a small amount of a binding agent (such as sodium chloride) and heating to 300–400°C. (Mentzel, B.P. 367598, 1930; Bartling, U.S.P. 1957129, 1934); the evolution of carbon dioxide from the bicarbonate gives the mass the necessary porosity. A further proposal is to start with raw carbonaceous matter (*e.g.* lignite or coal), which is mixed with sodium carbonate or bicarbonate and a binding agent, then briquetted and carbonised (Mentzel, G.P. 547694, 1930; Alterum Kredit A.-G., G.P. 604418, 1932); carbonisation in the presence of the alkali confers upon the coke an enhanced reactivity. It is claimed for activated masses of these types that they can be cyanised with nitrogen at temperatures as low as 830–

850°C., apparently in the absence of iron catalyst. It has already been mentioned that the Bucher process gives better results when the carbon and iron in the reaction mixture are in excess; A. Mentzel finds for his non-catalysed cyanising process that it is advantageous to use a 25–33% excess of carbon, the excess being added in the form of granules of diameter not more than 3 mm., to provide porosity and contact surface (G.P. 614100, 1930).

The fact that the cyanising reaction is reversible was proved by the experiments of Ferguson and Manning (Ind. Eng. Chem. 1919, **11**, 946). These authors heated mixtures of charcoal (1 part), iron (1 part), and sodium cyanide or carbonate (3 parts) with a range of definite mixtures of nitrogen and carbon monoxide. The composition of the product was independent of the nature of the solid raw materials, but varied with the temperature and the composition of the gas. At 946°C. a gas containing 5% carbon monoxide gave a solid product with 75% of the alkali cyanised, and one containing 48% CO a product with only 27·5% cyanised. At 1,000°C. the first gas mixture gave 80% cyanisation, and the second 59%. Ingold and Wilson (J.C.S. 1922, **121**, 2278) took precautions to avoid errors due to the volatilisation of sodium cyanide at these high temperatures, and found that, in the range 850–950°C., the relation between the composition of the liquid phase (Na_2CO_3 and $NaCN$) and the gaseous phase (CO and N_2) in equilibrium can be expressed by

$$\log\left(\frac{x^2}{1-x}\cdot\frac{(1-p)^2}{p}\cdot\pi^2\right)=23{\cdot}91-\frac{31{,}180}{T},$$

where x is the fraction of the sodium which is present as cyanide, p is the mol. fraction of nitrogen in the gas, and π is the total pressure.

The Bucher process was operated on a technical scale for a short time during 1918 by the Government of the United States, whose plant is described by Brown (Ind. Eng. Chem. 1919, **11**, 1010). The retorts were stationary nichrome tubes heated by producer gas, each tube having a life of 11–14 days and producing about 7½ lb./hour of sodium cyanide. Pure nitrogen from an air-liquefaction plant was used for the cyanising. The recovery of cyanide from the product by lixiviation with water is attended with the danger of ferrocyanide formation, though Chickering (Chem. Met. Eng. 1924, **31**, 967) describes such a method of obtaining anhydrous sodium cyanide from the product *via* the dihydrate. The method adopted at the plant in question was leaching with liquid ammonia under pressure. By this method unchanged alkali and carbon are left behind and can be reground with fresh raw materials for return to the retorts. Sodium cyanide of 92% purity was obtained from the liquid ammonia solution in the form of a white powder by evaporating off the ammonia in steam-heated evaporators, the ammonia loss being relatively low at 2 lb. per 100 lb. of cyanide made. A related process was worked between 1923 and 1927 by the California Cyanide Co. of Los Angeles. The retorts, made of nichrome or other nickel-chromium-iron alloy (B.P. 199900, 1922), were slightly inclined rotating tubes, 15 in. in diameter and having a length of 10 ft. heated to 950–1,050°C. (B.P. 202383, 1922). The charge consisted of a finely ground and granulated mixture of 54 parts of coke, 44 of sodium carbonate and 2 of iron (B.P. 136750, 1919), which passed down the tube in counter-current to the flow of nitrogen and was converted into a product containing 25–30% $NaCN$. As the primary object of this manufacture was the production of hydrocyanic acid, the solid product was treated with moist carbon dioxide (U.S.P. 1385335, 1385336, 1921), which was passed through the solid spread out on perforated trays:

$$2NaCN+H_2O+CO_2=Na_2CO_3+2HCN$$

In carrying out this reaction it is necessary to diminish the time of contact of the hydrocyanic acid with alkali, in order to minimise its decomposition and polymerisation. The product gases were dried and the hydrocyanic acid condensed by cooling. If desired, the dry hydrocyanic acid may be converted into sodium cyanide by reaction with sodium carbonate as described under Alkali Metal Cyanides, p. 481.

7. *From Nitrogen, Alkali Metals, and Carbon.*—The direct synthesis of potassium cyanide from its elements was first observed by Marchand (J. pr. Chem. 1850, **49**, 351) in testing for the presence of nitrogen in cast iron and steel by Lassaigne's method of heating the sample to red heat with potassium, extracting the product with water, and applying the Prussian blue test to the solution. Marchand found that, by repeated treatment of a sample of powdered iron, he was unable to exhaust the cyanide-forming reaction, and he showed that the cyanide was derived from gaseous nitrogen by carrying out the reaction in a closed tube containing nitrogen, which was completely absorbed. Since he was unable to prepare Prussian blue from the mixture of iron and carbon obtained by heating ferric succinate or benzoate, Marchand concluded that the carbon must be in chemical combination with the iron. At a later date, however, Remsen (Amer. Chem. J. 1881, **3**, 134) showed that iron powder loses its catalytic activity when superficially oxidised by exposure to air, and this may explain Marchand's failure with his simple mixtures of carbon and iron. Similar observations were made by Täuber (Ber. 1899, **32**, 3150).

Bucher in 1912 made use of the catalytic activity of iron in the synthesis of sodium cyanide from its elements (B.P. 11797 of 1913; U.S.P. 1082845, 1913; 1116559, 1914). The iron and the carbon are intimately mixed, and reaction with sodium and nitrogen proceeds at 500–1100°C. Bucher, like Marchand, believes that the iron acts as a solvent for the carbon, which is then capable of entering into reaction with sodium and nitrogen. In the cyanide synthesis from sodium carbonate (*see* previous section), Bucher postulates the initial formation from the carbonate and carbon of some metallic sodium, which is continually consumed by conversion into cyanide. This hypothesis makes the rate of cyanide formation dependent on the rate of solution of solid carbon in solid iron and, in view of the extremely rapid formation of cyanide actually observed, is hardly acceptable.

An early process of Castner (B.P. 12218 of 1894), in which molten sodium was allowed to flow downwards over a column of red-hot charcoal in an iron vessel, while a current of nitrogen was passing upwards through it, did not use the catalytic influence of iron. Castner abandoned it in favour of his synthesis from ammonia and sodium (p. 479), but it was further investigated by the Roessler and Hasslacher Co. in America at a later date. They found that a mixture of sodium vapour and nitrogen reacts with charcoal in the absence of iron above 650°C., and that the speed of the reaction above 800°C. is great enough to make the process commercially practicable (H. Philipp, Chem. Met. Eng. 1920, **22**, 313; U.S.P. 1249821, 1917; 1235887, 1917; 1332439, 1920). Similar proposals are contained in G.P. 368339, 1920, of Broch, who passes nitrogen under pressure through boiling sodium, and heats the vapour and gas under pressure with carbon in presence of an iron catalyst above the melting-point of sodium cyanide.

These processes have failed to displace or compete with the established Castner process on account of the great progress which has been made in the manufacture of synthetic ammonia.

8. *From Carbides and Nitrogen.*—Many proposals have been made for the production of sodium cyanide from carbides and nitrogen. They are all either variants of or closely related to the technically important process by which crude calcium cyanide is made from calcium carbide and nitrogen through the intermediate compound calcium cyanamide, and are therefore described in the section dealing with this process (Alkaline Earth Cyanides, p. 487).

PROPERTIES OF THE ALKALI METAL CYANIDES. **Potassium cyanide, KCN,** crystallises in anhydrous, colourless octahedra from aqueous solutions, or in cubes from the molten salt. The specific gravity of the solid is 1·52. It melts at a dull red heat, and volatilises without decomposition at high temperatures. It is readily soluble in water ; the saturated solution at 25°C. contains 71·2 g. **KCN** per 100 g. of water (Bassett and Corbet, J.C.S. 1924, **125**, 1660), and at the boiling-point (103·3°C.) 122·2 g. per 100 g. of water. Dry ethyl alcohol dissolves 1·9 g. **KCN** per litre, methanol 30 g. per litre at 25° (Thompson, U.S. Bur. Standards, J. Research, 1931, **6**, 1051). It is moderately soluble in anhydrous ammonia; according to Johnson and Krumboltz (Z. physikal. Chem. 1933, **167**, A, 249), 4·55 g. of **KCN** dissolve in 100 g. of ammonia at–33·9°. The salt deliquesces in moist air.

When a mixture of potassium cyanide and soda lime is heated in air at 270°C., 23% of the cyanide is oxidised to nitrate; silver and nickel assist the oxidation catalytically, the yields of nitrate being 65 and 71% respectively with these metals. The oxidation of cyanide to cyanate by alkaline permanganate is accelerated, and secondary reactions are suppressed, by copper sulphate (Gall and Lehmann, Ber. 1928, **61**, [B], 670). Potassium cyanide reacts with tetrathionate in aqueous solution to form thiocyanate, sulphate and thiosulphate; the reaction velocity has been measured by Ishikawa (Z. physikal. Chem. 1927, **130**, 73), and the effect of varying the p_H value of the reacting solution by Foresti (Atti soc. ital. progresso sci., 1934, **22**, No. 2, 263; Z. anorg. Chem. 1934, **217**, 33):

$$S_4O_6''+CN'+2OH' = S_2O_3''+SO_4''+CNS'+H_2O$$

This reaction is of physiological importance in connection with the use of tetrathionate as an antidote in cyanide poisoning.

A phase rule study of the double salts of potassium cyanide with the cyanides of copper, silver, gold and thallium has been made by Bassett and Corbet (J.C.S. 1924, **125**, 1660), and with those of zinc, cadmium, mercury and nickel by Corbet (*ibid.* 1926, **129**, 3190).

Sodium cyanide, NaCN, crystallises from the molten salt in anhydrous, apparently cubic crystals. From aqueous solutions below 35°C. large colourless plates of the dihydrate, $NaCN,2H_2O$, are deposited. Joannis (Ann. chim. phys. 1882, [v], **26**, 484) obtained a hydrate $NaCN,\frac{1}{2}H_2O$ from cold 85% alcohol. The dihydrate decomposes at 34·7°C. into the anhydrous salt and a saturated solution, about 40% of the sodium cyanide separating in the anhydrous state. The solubility of the dihydrate in water is as follows (in g. **NaCN** per 100 g. of water):

Temp. °C.	−20	0	20	34·7
Solubility .	35·4	43·4	58·3	82

The solubility of the anhydrous salt is almost independent of the temperature at 82 g. per 100 g. of water.

Dry ethyl alcohol dissolves 9·7 g. **NaCN** per litre, and methanol 78 g. per litre at 25° (Thompson, U.S. Bur. Standards, J. Research, 1931, **6**, 1051). The solubility in aqueous methanol is given below in g. **NaCN** per litre of solution:

	% Methanol by weight.			
Temp. °C.	100	70·9	61·4	50
16	67·9	131	207	231
31	63·3	142	—	272

100 g. of anhydrous ammonia dissolve 114·5 g. of sodium cyanide at −12° to −25°C. At lower temperatures a compound $NaCN{\cdot}5NH_3$ separates in large flat plates resembling the dihydrate. The solid ammoniate is in equilibrium with solutions of the following composition (unpublished work by T. Ewan):

Temp. °C.	Liquid phase, g. NaCN per 100 g. NH_3.	
−31	57·7	57·7
−32	43	75
−33	40	80
−34	34	88
−39	21	—

Sodium cyanide (96%) melts at 540°C. Ingold (J.C.S. 1923, **123**, 885) has measured the vapour pressure at various high temperatures:

Temp. °C.	800	900	1000	1100	1200	1300	1360
Vap. press. (mm.)	0·76	3·43	12·4	36	89·8	204	314

The boiling-point is 1,500°C., and the latent heat of evaporation 37 kg.-cals. per g.-mol. The pure salt, when heated in dry air free from carbon dioxide, is stable at temperatures up to 370°C. Rapid oxidation occurs, however, in the presence of iron or nickel or their oxides, with formation of cyanate, carbonate and carbon dioxide. Sodium cyanate is the primary product, which is itself rapidly oxidised to carbonate and carbon dioxide in the presence of nickel :

$$2NaCNO+3O=Na_2CO_3+CO_2+N_2$$

R. Höltje (Z. anorg. Chem. 1933, **214**, 65) has investigated the changes occurring in melts of sodium cyanide and sodium hydroxide. In the absence of water and oxygen, reaction only occurs above 500°C., and the products are carbonate, cyanamide and hydrogen. If a little water is present, decomposition starts at 300°C. with saponification to ammonia and formate, the latter being converted into carbonate and hydrogen. Nitrogen, carbonate, and nitrate are produced in the presence of oxygen.

Sodium cyanide absorbs moisture from the atmosphere. It has been found to take up water from air which has been saturated with aqueous vapour at 20°C. at all temperatures below 44°C. Care is therefore necessary in taking samples of the salt for analysis. Dilute solutions of sodium cyanide slowly decompose in contact with air, the hydrocyanic acid formed in the solution by hydrolysis being lost by evaporation and thus allowing the decomposition to proceed further. Carbon dioxide absorbed from the atmosphere also displaces hydrocyanic acid with a similar result. At higher temperatures, for instance, during the evaporation of solutions, saponification to ammonia and formic acid may occur. Data on the rate of hydrolysis of potassium cyanide solutions under various conditions are given by Novalevitsch (Ukrain. Chem. J. 1934, **8**, Wiss. tech. Teil, 226) and Wick (Quart. Rev. Amer. Electroplaters' Soc. 1933, **19**, No. 10, 20). When strong sulphuric acid is present, the formic acid initially produced by the saponification is immediately decomposed into carbon monoxide and water.

In the presence of oxygen, sodium cyanide dissolves almost all metals with the exception of lead and platinum. In the case of iron, which Liebig found to dissolve in cyanide with production of ferrocyanide and hydrogen, it is necessary for the iron to be in a finely divided form, since iron vessels are used in the technical handling of hot, concentrated cyanide solutions without serious corrosion. Zinc is slowly dissolved without oxygen, but more rapidly when it is present.

Uses of Sodium Cyanide.—The most extensive use of sodium cyanide is in the extraction of gold and silver from their ores, and this subject is dealt with under Gold Cyanides, p. 486. Another use of the alkali metal cyanides is in electroplating, which is mentioned under Silver Cyanide, p. 487. Other applications are as follows :

(i) *Case-hardening.*—When a soft steel, usually containing about 0·15% carbon, is immersed in a bath of fused sodium cyanide at 800–900°C., both carbon and nitrogen are taken up superficially in the form of a solid solution of the carbide, Fe_3C, and the nitride, Fe_2N, in γ-iron. When the steel is cooled very rapidly this is changed into a supersaturated solution of these substances in α-iron, which is extremely hard; the underlying metal remains unchanged. The composition of the hardened skin may be controlled by diluting the cyanide bath with sodium carbonate, a bath rich in cyanide giving a higher carbon content, and the thickness of the skin by varying the time of immersion; 1 hour at 900°C., for example, gives a penetration of 0·4 mm. (Beilby and Nelson, J.S.C.I. 1932, **51**, 149T). Bucher showed (Ind. Eng. Chem. 1917, **9**, 236) that the reversible decomposition of cyanide according to the equation

$$2NaCN \rightleftharpoons 2Na+2C+N_2$$

takes place in the presence of iron ; cyanide and pure iron give carbon and nitrogen by decomposition, which combine with the iron, whereas carburised iron with sodium and nitrogen gives cyanide.

(ii) *Froth Flotation.*—In 1922 Sheridan and Griswold (U.S.P. 1427235, 1421585) showed that zinc blende and galena may be separated by carrying out the known froth flotation process in an alkaline solution containing sodium cyanide. Only 0·1–0·2 lb. of sodium cyanide per ton of ore is required to prevent the flotation of the zinc blende, that of the galena being unaffected. The process may also be applied to the separation of the crystalline sulphides of copper and iron, cyanide acting as a depressant for the iron. A discussion of the mechanism of flotation is given by Brighton, Burgener and Gross (Eng. and Min. J. 1932, **133**, No. 5, 276). The action of certain sulphur-containing compounds in promoting the collection of minerals in the froth appears to be connected with their ability to form films of insoluble heavy metal salts at the mineral-solution-air interface, and the action of cyanide in destroying the collecting action is said to be due to the solvent action of cyanide on the collecting films. It is also suggested that, where pyrite is present, the formation of ferro- and ferri-cyanides may contribute to the depressing effect ; these compounds might become adsorbed at the surfaces, and might also change the polarity of the charge adsorbed on the sulphide surface.

III. HEAVY METAL CYANIDES.

In this section is given a brief account of the preparation and properties of the technically important heavy metal cyanides.

Copper cyanide.—The only stable cyanide of copper is cuprous cyanide, $Cu_2(CN)_2$. When potassium cyanide is added to cupric salt solution, a brownish precipitate of cupric cyanide, $Cu(CN)_2$, is first formed, which gradually evolves cyanogen and changes into green cupric cuprocyanide. On heating, this complex salt loses a further quantity of cyanogen and yields white cuprous cyanide, which resembles silver cyanide in constitution and reactions. It may also be produced by the action of sodium cyanide on a solution of cuprous chloride in sodium chloride solution, when no cyanogen is lost.

Cuprous cyanide is soluble in solutions of the alkali metal cyanides, about 2·5 mols. of KCN being required to dissolve 1 mol. of $CuCN$; the solutions contain the complex anions $Cu(CN)_3''$ and $Cu(CN)_4'''$ according to Kunschert (Z. anorg. Chem. 1904, **41**, 359), but Britton and Dodd (J.C.S. 1935, 100) were only able to find $Cu(CN)_2'$, their conclusion being based on measurements of the HCN-vapour pressure over the solution, the p_H value, and the electrical conductivity of the solution. The complex anion is exceedingly stable, its dissociation into cuprous ions being so slight that no cuprous sulphide is precipitated from the solution by sulphuretted hydrogen. For this reason copper in the presence of oxygen, and all copper compounds, dissolve readily in cyanide solutions. Solutions of sodium and potassium cuprocyanides are used in the electrodeposition of copper on iron.

Gold cyanides.—Aurous cyanide, $AuCN$, is a yellow crystalline powder, insoluble in water and mineral acids, which is formed by the action of hydrocyanic acid on auric hydroxide, or by warming potassium aurocyanide with hydrochloric acid and evaporating the solution to dryness, washing the residue with water. It is readily soluble in solutions of the alkali and alkaline earth cyanides, giving complex aurocyanides such as $KAu(CN)_2$. A solution of the potassium salt is used for electroplating with gold, and may readily be made by precipitating a solution of gold chloride with ammonia and dissolving the fulminating gold in a solution of potassium cyanide, or by precipitating gold chloride with magnesia, dissolving out the excess of magnesia in the precipitate with nitric acid, and then dissolving the auric hydroxide in potassium cyanide as before.

Sodium aurocyanide is technically important because it is formed when finely divided gold is dissolved in a solution of sodium cyanide in the presence of oxygen or other oxidising agent:

$$\begin{aligned}&4NaCN+2Au+\tfrac{1}{2}O_2+H_2O\\&\qquad=2NaAu(CN)_2+2NaOH\end{aligned}$$

Gold is one of the noblest metals and comes below hydrogen in the electro-potential series. Hence when gold is in contact with water or acids, equilibrium in the reaction

$$2Au+2H^+\rightleftharpoons 2Au^++H_2$$

is reached at infinitesimal concentrations of aurous ion. The effect of cyanide in causing the solution of some metals, for example, iron and copper, in water is due to the formation of little dissociated complex metal cyanide ions, which continually reduces the concentration of the simple kation and causes the dissolution reaction to proceed. In the case of gold, however, the equilibrium concentration of aurous ion is so vanishingly small that the formation of aurocyanide ion is not in itself sufficient to promote the dissolution of the metal, even though the complex ion, as stated below, is extremely stable and little dissociated. It is necessary, in addition, to remove the hydrogen liberated by the solution reaction, by having present an oxidising agent such as dissolved oxygen or hydrogen peroxide. Ionically, therefore, the reaction by which gold dissolves in aerated cyanide solution may be represented as follows:

$$2Au+4CN'=2Au(CN)_2'+2\ominus$$

$$H_2O+\tfrac{1}{2}O_2+2\ominus=2OH'$$

The dissociation of the complex aurocyanide anion into aurous and cyanide ions is very slight, and smaller than the dissociation of the complex silver and mercury cyanide ions. Thus, although free gold is electro-negative to both silver and mercury, and would be displaced by them from solutions of simple aurous salts, gold in cyanide solutions is electropositive to these metals, and displaces them from their solutions in cyanide. In the case of a more electropositive metal such as zinc, on the other hand, the difference in the solution tendencies of the free metals is too great for the stability of the complex aurocyanide ion to cause a reversal of the normal relation, and zinc readily displaces metallic gold from aurocyanide solutions with the formation of a complex zinc cyanide:

$$2Au(CN)_2'+Zn\rightleftharpoons Zn(CN)_4''+2Au$$

In the technical extraction of gold from its ores, the ground ore is leached with alkaline cyanide solution of approximately 0·05% strength, and the gold is precipitated from the resulting aurocyanide solution by treatment with zinc shavings or finely divided zinc dust. There are frequently present in the ore quantities of iron, copper and zinc sulphides which increase the cyanide consumption in the dissolution process by converting cyanide into complex cyanides and thiocyanate. In order to reduce the loss of cyanide by this degradation, it is advisable to use cyanide solutions of lower strength, but a limit to the reduction of strength of the leaching solution is set by the fact that it causes incomplete precipitation of the gold from the pregnant cyanide solution by the zinc. In current practice at the reduction plants of the Rand goldfield, the cyanide consumption averages 0·25 lb. $NaCN$ per ton of ore treated.

Numerous proposals have been made for the recovery of the cyanide rendered unavailable by reaction with iron, copper, zinc and sulphur in the ore. Mills and Crowe (B.P. 241669, 1924) would acidify the solution leaving the zinc boxes (after precipitation of the gold) with sulphur dioxide, and remove the hydrocyanic acid from it by a current of air. The hydrocyanic acid is re-absorbed from the air in alkali. Leaver and Woolf (Amer. Inst. Min. Met. Engs., Tech. Publ. 205, 1929) propose to acidify the solution and then to precipitate copper and zinc with sodium sulphide; after the addition of lime to the filtered solution it is re-used. R. M. P. Hamilton describes a process whereby zinc sulphate is added to the barren solution, throwing down a mixture of zinc and cuprous cyanides, this is boiled with dilute sulphuric acid, liberating hydrocyanic acid which is absorbed in milk of lime for return to the cyanidation process, and regenerating the zinc sulphate (Eng. and Min. J. 1932, **133**, No. 1, 53). In B.P. 416475, 1932, it is proposed to treat the gold-bearing cyanide solution with a cuprous salt, which gives a precipitate consisting essentially of cuprous cyanide and the cuprous salts of the complex cyanides of the precious and other metals ; this precipitate is treated with sulphuric acid to liberate hydrocyanic acid equivalent to all the complex cyanides, leaving a residue containing the precious metals and cuprous thiocyanate, from which the latter is removed by roasting to copper oxide and leaching with acid. The copper solution may be re-used in the process.

Auric cyanide, $Au(CN)_3{\cdot}HCN{\cdot}1\frac{1}{2}H_2O$, is formed on treating potassium auricyanide with hydrofluosilicic acid.

Mercuric cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in excess of hydrocyanic acid and evaporating to crystallisation. It crystallises in anhydrous, colourless crystals of sp.gr. 4·0. It is soluble in water to the extent of 93 g. per litre at 20°C., and 530 g. per litre at 100°C. The solubility in ethyl alcohol is 10·1 g. per 100 g. at 19·5°C., and in methanol 44·2 g. per 100 g. at the same temperature. The electrolytic dissociation of mercuric cyanide in aqueous solution is extremely small, so that mercuric cyanide can be formed, for instance, by boiling mercuric oxide with Prussian blue; this shows that its dissociation is even less than that of the ferrocyanides into cyanide. It is not decomposed by caustic alkalis, and only gives hydrocyanic acid on boiling with strong acids. Sulphuretted hydrogen does, however, precipitate the extremely insoluble mercuric sulphide from its solution. The reaction of mercurous salts with cyanides yields mercuric cyanide and mercury, instead of the expected mercurous cyanide. On heating to 400°C., mercuric cyanide decomposes into mercury and cyanogen.

Small quantities of mercuric cyanide are sometimes used in addition to alkali cyanide in the treatment of ores containing silver sulphide (Clennel, "Cyanide Handbook," London, 1910, p. 297). By its use the dissolution of silver sulphide is accelerated, probably owing to the formation of mercuric sulphide by the reaction :

$$Hg(CN)_2+Ag_2S+2KCN = HgS+2KAg(CN)_2$$

Silver cyanide, $AgCN$, is formed by precipitation of silver salt solutions with hydrocyanic acid, or alkali cyanide solution not in excess. It forms a white, cheesy precipitate which is stable to light. Its solubility in water at 25°C. is $4{\cdot}4\times10^{-6}$ g.-mols. per litre, intermediate between the thiocyanate (less soluble) and the chloride. It is hardly attacked by cold, dilute nitric acid, but is decomposed quantitatively on boiling (Plimmer, J.C.S. 1903, **83**, 285). It is slightly soluble in an aqueous solution of hydrocyanic acid, forming the unstable complex acid $HAg(CN)_2$, and dissolves readily in alkali cyanide solutions to give alkali salts of this acid, which are very stable. The electrolytic dissociation of the complex $Ag(CN)_2'$ ion is so small that all silver salts, except the sulphide, are dissolved by cyanide solutions; the sulphide and the free metal require the presence also of oxygen for their dissolution (*see under* Gold Cyanides, p. 486). The soluble salt $KAg(CN)_2$ is used for electroplating, fulfilling the requirement of producing a tenacious deposit of the proper consistency by reason of the fact that its solutions have a very small concentration of free Ag^+ ions; to obtain the same conditions with simple silver salts, very dilute and highly resistant solutions would have to be used. The view is held that silver cyanide itself is to be regarded as the silver salt of the acid $HAg(CN)_2$.

On heating in the dry state, silver cyanide gives off about one-half of its cyanide in the form of cyanogen $(CN)_2$, and on further heating in the presence of oxygen gives metallic silver containing some carbon.

Zinc cyanide, $Zn(CN)_2$, may be prepared by precipitating zinc acetate solution with hydrocyanic acid vapour. It is also formed by the action of hydrocyanic acid on zinc oxide, but is difficult to prepare in the pure state owing to the ease of its partial decomposition by water. It is a white substance, insoluble in water but soluble in acids and in cyanide solutions. The dry salt decomposes only at a bright red heat.

Complex cyanides, in which the zinc appears in the anion, are formed when zinc cyanide dissolves in alkali cyanide solutions. The complex zinc cyanide ions are much less stable than those containing copper, gold, silver and mercury, and zinc sulphide is precipitated by a small excess of alkali sulphide. The potassium salt, $K_2Zn(CN)_4$, crystallises from aqueous solution in large, well-formed octahedra, the solubility of which is 11 g. per 100 g. of water at 20°C. It is fusible at a red heat without decomposition. The sodium salt, $NaZn(CN)_3$, $2\frac{1}{2}H_2O$, is readily soluble in water.

Barium platinocyanide,

$$BaPt(CN)_4,4H_2O,$$

is made by electrolysing a solution of barium cyanide (270 g. per litre) between platinum electrodes with an alternating current at a current density of 0·4 amperes per sq. cm. About 0·6 g. of platinum is dissolved per ampere-hour. After removing the excess of barium by means of carbon dioxide, the solution is concentrated to crystallisation (Brochet and Petit, Bull. Soc. chim. 1904, [iii], **31**, 630). The salt crystallises in monoclinic prisms, which are yellow by transmitted, and violet-blue by reflected light. It dissolves in 33 parts of water at 16°C. By recrystallisation from a solution containing barium cyanide, it is obtained in small crystals which are highly fluorescent when exposed to X-rays, and are suitable for making fluorescent screens for X-ray work.

IV. ALKALINE EARTH CYANIDES

TECHNICAL METHODS OF PREPARATION.—1. *From Carbides and Nitrogen.* The direct absorption of nitrogen by the metallic carbides might be expected to yield cyanides, and a considerable amount of work has been done on the nitrogenation of carbides with the object of cyanide production. The alkali metal carbides have not been closely investigated, but Frank and Caro (B.P. 15066 of 1895) noted that they absorbed nitrogen at a " dark red heat " to form cyanides. It is possible that the formation of cyanide from alkali carbonate, carbon and nitrogen (*see under* Alkali Metal Cyanides, p. 481) may proceed by the primary formation from carbonate and carbon of a carbide, which is subsequently nitrogenated to cyanide, as was first suggested by Hughes (Report of Juries, Exhib. of 1851, **1**, 95).

The absorption of nitrogen by the alkaline earth carbides has been extensively studied. Moissan (Compt. rend. 1894, **118**, 503, 684) could find no appreciable reaction between pure, dry nitrogen and the pure carbides, except that the product from barium carbide yielded traces of ammonia on boiling with water. In 1895 Frank and Caro (B.P. 15066 of 1895) discovered that the impure carbides absorb nitrogen, that the product in the case of barium carbide consists largely of the corresponding cyanide, but that the result with calcium carbide was " unsatisfactory." Similar results were independently obtained at the same time by Willson (B.P. 21997 of 1895), who suggested in the case of calcium that a more complicated nitrogen compound is formed. The fact that a large part of the combined nitrogen in nitrogenated calcium carbide (and a smaller part in the case of barium carbide) is in the form of a cyanamide salt was discovered by F. Rothe, working under Frank's direction (Frank and Caro, B.P. 25475 of 1898; Rothe, Z. angew. Chem. 1903, **16**, 658).

Frank and Caro's first attempts at the technical production of cyanides were naturally made with barium carbide, which was finely ground and heated with pure nitrogen to 700°C. A product containing about 11% of nitrogen was obtained, of which 30% was present as barium cyanide and the rest as barium cyanamide. In order to convert the cyanamide into cyanide, the material was heated with dry sodium carbonate and carbon, when the following reactions may have occurred :

$$BaNCN+Na_2CO_3=BaCO_3+Na_2NCN$$

$$Na_2NCN+C=2NaCN$$

Proposals to obtain marketable sodium cyanide from this product by extracting the sodium cyanide with water, converting it into ferrocyanide, and then fusing it with sodium by the Erlenmeyer process already described (p. 478) failed on economic grounds (Erlwein, V. Intern. Kongress angew. Chem., Berlin, 1903, I, 646). Attention was therefore turned to calcium carbide, which absorbs nitrogen at about 1,100°C., giving a product containing 20–23·5% nitrogen, which is wholly in the form of calcium cyanamide, and about 12% of carbon :

$$CaC_2+N_2=CaNCN+C$$

(For details of the manufacture of calcium cyanamide, *see* Calcium, Vol. II, p. 219). When this product is heated with sodium chloride, the cyanamide is largely converted into cyanide (Erlwein, *l.c.* ; Erlwein and Frank, U.S.P. 708333 of 1902). Large-scale experiments were carried out up to 1914 in Germany with little success. Using 2–3 parts of salt and 1 part of cyanamide at a maximum temperature of 960°C., from 40 to 75% of the nitrogen was obtained in the form of cyanide (Landis, Chem. Met. Eng. 1920, **22**, 265). The technical failure was probably due to the short life of the furnace refractories, the use of unsuitable gas-heating, and the occurrence of frothing in the mass due to the liberation of nitrogen.

The technique of the process was considerably improved by Landis at a plant erected at Niagara by the American Cyanamid Co. Rationally designed furnaces were used with electrical heating, and the frothing referred to above was prevented by the addition of small quantities of carbide. The operating temperature was raised to 1,300°C. with marked improvement of the yields (Eastman, U.S.P. 1282395, 1918), and the importance of quickly cooling the fused reaction mass was realised from the observation that a reversion of cyanide to cyanamide occurs between 400° and 700°C. (Freeman, U.S.P. 1282405, 1918). A mixture of 1 part of crude calcium cyanamide with 0·8 part of salt and 0·05–0·10 part of calcium carbide is fed into a single-phase electric furnace of the arc resistance type with conducting hearth and a single suspended electrode. The mixture fuses, and is run off almost continually into a pan in which an internally water-cooled drum rotates, taking up a thin layer of the fused material which solidifies and is scraped off in thin flakes. The efficiency on nitrogen is approximately 90%, and the grey flakes or powder in which the product is marketed have the following analysis : $Ca(CN)_2$ 45·0%, $NaCl$ 31·9%, $CaCl_2$ 1·2%, SiO_2 0·9%, Fe_2O_3 and Al_2O_3 2·0%, $CaCN_2$ 1·8%, carbon 2·8%, CaC_2 1·9%, CaO 11·8%, CaS 0·9%.

The mechanism of this cyanide-forming reaction was at first imperfectly understood. The effect of salt in accelerating the transformation of cyanamide into cyanide is illustrated by the data of W. S. Landis (U.S.P. 1359257, 1920), who heated various mixtures of cyanamide and salt to a temperature above 1,300°C., and then cooled them rapidly to below 400°C., with the following results :

Original Mixture.			Product.
Cyanamide.	Salt.	CaC_2	%NaCN
200	180	5	36·5
200	100	7	45·0
200	45	9	50·0

Pascal and Bernheim (Compt. rend. 1931, **192**, 1425) also found that the yield of cyanide at a given temperature increases with increase in the proportion of salt, though not markedly above a molar ratio $NaCl/CaCN_2$ of 2. The optimum proportion of charcoal was 0·2 parts to 1 of cyanamide, which corresponds closely with that actually present in technical crude cyanamide. These results might be explained by writing the fusion reaction as

$$CaNCN+C+2NaCl=CaCl_2+2NaCN,$$

and Perret and Perrot (Compt. rend. 1933, **197**, 764), who studied the reverse of the above reaction, suggest that in the crude cyanide obtained by the Landis process the cyanide is combined with sodium rather than with calcium. According to Freeman (Can. P. 229767, 1923), however, the salt/cyanamide ratio in the initial mixture is without influence on the equilibrium yield of cyanide produced in the fusion, and the use of only half the quantity of salt required by the above equation is actually recommended.

Landis (U.S.P. 1359257, 1920) had already shown that cyanide formation does occur in the absence of salt, and Franck and Neubner (Z. Elektrochem. 1934, **40**, 693) investigated in detail the unassisted reaction between barium cyanamide and carbon, finding increasing cyanide production as the temperature was raised. In the case of calcium cyanamide the relationships are more complicated, and the presence of a flux, preferably a calcium salt such as the chloride or fluoride, is of great advantage. It appears reasonable to assume, with Franck and Burg (*ibid.* 1934, **40**, 686), that the reaction occurring during the fusion is

$$\mathrm{CaNCN + C \rightleftharpoons Ca(CN)_2} - 38{\cdot}5 \text{ kg.-cal.,}$$

an endothermic reaction which goes further to the right at higher temperatures (*see also* Franck and Bank, *ibid.* 1934, **40**, 699). In addition, the slightly endothermic double decomposition,

$$\mathrm{Ca(CN)_2 + 2NaCl \rightleftharpoons 2NaCN + CaCl_2} - 3{\cdot}9 \text{ kg.-cal.,}$$

of which the equilibrium will be little affected by temperature change, may proceed to a small extent. On this view, the crude cyanide obtained from technical cyanamide by fusion with salt consists essentially of a mixture of calcium cyanide and sodium chloride, a conclusion confirmed by an X-ray analysis of the product carried out by Bredig (*see* Franck *et al.*, Samml. chem. chem.-techn. Vorträge N.F. No. 6, 1931). The conclusion is also in agreement with the general properties of the product, such as its non-hygroscopic character (indicating the absence of calcium chloride) and the rate of its hydrolysis by atmospheric moisture to give hydrocyanic acid.

Crude calcium cyanide is used in gold-mining and in fumigation, but cannot be used in the case hardening of iron and steel. It is at a general disadvantage compared with high-grade fused sodium cyanide on account of its relatively low cyanide strength, and efforts have been made both to convert it into a high-grade product and to modify the synthesis reaction so as to produce a high-grade product directly. Although the desired products are in most cases sodium cyanide, the processes are dealt with at this point, and not under Alkali Metal Cyanides, because of their basic derivation from the Landis process.

In U.S.P. 1734562, 1929, Cooper proposed to recover sodium cyanide from the crude calcium cyanide by mixing it with sodium carbonate and dissolving the mixture in water to give a solution of sodium cyanide and sodium chloride, which was concentrated to a strength of 20% NaCN, and then cooled to −15°C. to crystallise the dihydrate $\mathrm{NaCN,2H_2O}$. This was dried by centrifuging, and converted by heating into the anhydrous salt, analysing 80–90% NaCN. This process has not been brought into commercial operation.

An interesting variation of the Landis process is provided by E. J. Pranke, who proposes (U.S.P. 2004130, 1935) to fuse calcium cyanamide with powdered sodium cyanide at 1,350–1,400°C. in an electric furnace; as in the Landis process, the reaction $\mathrm{CaNCN + C = Ca(CN)_2}$ occurs, but in the presence of sodium cyanide a stable double salt $\mathrm{Na_2Ca(CN)_4}$ is formed, which is preserved by rapid cooling. The product as it stands has a cyanide strength equivalent to 80% NaCN and if desired can be converted into pure sodium cyanide by treating with liquid ammonia. Sodium cyanide is dissolved out, and can be recovered by evaporation of the solvent (U.S.P. 1947570, 1934), and calcium cyanide is left, and can be converted into the sodium salt by a method similar to that described in the preceding paragraph (*see also* B.P. 411177, 1932). In several other patents (*e.g.* Canad.P 319011, 1932), Pranke claims the production of the double salt from calcium carbide, sodium chloride, and nitrogen, a procedure which constitutes a combination of the cyanamide synthesis and the Landis cyanide fusion reaction in one step, giving a direct nitrogenation of carbide to cyanide. The direct nitrogenation of calcium carbide to cyanide at 1,240°C., with 4% of calcium fluoride as a flux, has been reported by Franck (Samml. chem. chem.-techn. Vorträge N.F. No. 6, 158), who obtained an 85% yield of cyanide (*see also* G.P. 588943, 1928).

The use of sodium carbonate as a flux instead of sodium chloride is stated by Wöhler, Krall and Dornhöfer (Angew. Chem. 1934, **47**, 733) to lead to the conversion of commercial calcium cyanamide into sodium cyanide, the reaction being:

$$\mathrm{CaNCN + C + Na_2CO_3 = CaCO_3 + 2NaCN}$$

Whether sodium cyanide is formed during the fusion may be uncertain, but it is obvious that when the product is extracted with water, sodium cyanide solution will be obtained and calcium carbonate left behind. According to B.P. 437614, 1934, fusion of the mass is not necessary, as the reaction proceeds under suitable conditions at 600–1,100°C., and the granular product is then more expeditiously leached with water.

Considerable technical advantages are claimed by D. Hatt (Chim. et Ind. 1932, **28**, 777) for a modification of the Landis process which has been investigated semi-technically in France by the Usines de Produits chimiques de Thann. The new process consists in the treatment of calcium cyanamide with a mixture of two substances which react strongly exothermically to give nascent carbon, *e.g.* calcium carbide and sodium carbonate (G.P. 480905). The production of carbon is said to proceed as follows:

$$\mathrm{Na_2CO_3 + 2CaC_2 = Na_2O + 2CaO + 5C}$$

and the whole reaction thus:

$$\mathrm{CaNCN + 2CaC_2 + Na_2CO_3 = 2NaCN + 3CaO + 4C}$$

The reaction is exothermic, and starts at 450–500°C., after which the temperature rises spontaneously to 920°C. within 9 minutes. The crude product contains 20–22% $NaCN$, and sodium cyanide of 99% purity can readily be produced from it by extraction with liquid ammonia. The crude product of this process is remarkable in that its cyanide content is easily and quantitatively hydrolysed by steam at atmospheric pressure into sodium formate and ammonia.

So far as is known, none of these modifications to the Landis process has been developed commercially.

2. *From Carbonates and Nitrogen.*—It is evident, from the descriptions already given of methods of fixing nitrogen in the form of alkali and alkaline earth cyanides, that compounds of the alkaline earth metals are more suitable than those of the alkali metals for fixing atmospheric nitrogen and that, of the alkaline earth metals, the compounds of barium most readily form cyanides under the conditions necessary for nitrogen absorption. Margueritte and A. L. de Sourdeval (B.P. 1171 of 1860; Compt. rend. 1860, **50**, 1100) discovered that a mixture of barium oxide and carbon readily absorbs nitrogen on heating, and gives barium cyanide. Ludwig Mond (B.P. 433 of 1882; J.S.C.I. 1889, **8**, 505) also worked on this process, using a mixture of barium carbonate and excess of carbon briquetted with pitch: cyanide formation was appreciable at 1,200°C., and proceeded most readily at 1,400°C. The apparatus used was similar to that of Possoz and Boissière in their analogous process with sodium carbonate (*see under* Alkali Metal Cyanides, p. 481), and 40% of the barium was cyanised. In each of the above cases the object of the experiments was the production of ammonia.

As in the technical practice of the Bucher and Landis processes, therefore, internal electrical heating is very suitable. Readman developed such a process (B.P. 6621 of 1894), which was worked by the Scottish Cyanides Co. between 1899 and 1907. Barium carbonate from a later stage was mixed to a thick paste with ground coal, dried and coked in ordinary gas retorts. The granular mixture of barium oxide and coke so produced passed to a cylindrical electric furnace, the lower part of the wall forming one electrode and a central carbon rod suspended in the upper part of the furnace forming the other. The solid mass was heated in passing downwards between the electrodes, and a current of producer gas containing 70% of nitrogen was passed upwards through the mass. The cooled product was lixiviated with water, and the solution of barium cyanide, cyanamide and hydroxide treated with sodium bicarbonate. After filtering off the barium carbonate precipitate for return to the process, the sodium cyanide solution was concentrated *in vacuo*, cooled to deposit crystals of $NaCN,2H_2O$ which were centrifuged and dehydrated by heating. The Badische Anilin und Soda Fabrik also developed this process (G.P. 190955, 1906), obtaining a fusion product containing 60% of its fixed nitrogen as barium cyanide and 40% as cyanamide. This was treated with acetylene at 600–800°C., when the cyanamide was transformed into cyanide. An account of more recent work on the process in Sweden is given by Stålhane and Liander (Ing. Vetenskaps Akad. Handl. No. 112, 1931, 5–60).

A considerable amount of work on the chemistry of this method of nitrogen fixation as cyanide has been done at lower temperatures. Bertelsmann (Technologie der Cyanverbindungen, 1906, 83) has ascribed the ease of nitrogenation of barium compounds to their infusibility, so that they remain solid and present a large surface to the action of nitrogen under the cyanising conditions. But although undecomposed barium carbonate does not melt at 1,350°C. (Finkelstein, Ber. 1906, **39**, 1585), its mixtures with barium oxide, which are always formed at the high temperatures in question, are readily fusible. The formation of barium cyanide (m.p. about 600°C.) still further increases the fusibility of the reaction mixture, which must therefore in this process be a liquid phase of variable composition.

Kühling and Berkhold (Ber. 1908, **41**, 28) obtained 40% nitrogenation of the barium in a mixture of barium carbonate and carbon at 1,150°C., the reaction diminishing as the temperature was lowered and being extinguished at about 925°C. Ewan and Napier (J.S.C.I. 1913, **32**, 467) showed that nitrogen absorption which, as stated by Mond (*l.c.*) depends on the two reversible reactions,

$$BaCO_3+C \rightleftharpoons BaO+2CO-101{\cdot}2 \text{ kg.-cal.}$$
$$BaO+3C+N_2 \rightleftharpoons Ba(CN)_2+CO-43{\cdot}1 \text{ kg.-cal.}$$

is therefore hindered by the accumulation of carbon monoxide, and favoured by the use of a large excess of nitrogen. In 2 hours at 960° C. they obtained 40% nitrogenation of the barium when using a 28-fold excess of nitrogen. The pressure of carbon monoxide in equilibrium with pure barium carbonate and carbon is large enough to prevent the second reaction from proceeding to the right, but as the barium carbonate is diluted with barium oxide the equilibrium pressure falls to very low values. It is therefore concluded that the greater part of the barium carbonate decomposes before any cyanide is formed. Ewan and Napier obtained the same equilibrium product, at a given temperature and gas composition, from starting mixtures of $BaCO_3+BaO+C$ and of $Ba(CN)_2+BaCN_2+C$. Their results at temperatures of 1,000°, 1,100°, and 1,150°C. with various mixtures of nitrogen and carbon monoxide appeared to indicate by extrapolation that the maximum quantity of barium which could combine with pure nitrogen was 50% at all the temperatures, but they obtained a product corresponding to 57·1% nitrogenation by heating for 82 hours at 1,100°C. with nitrogen containing only 0·1% carbon monoxide.

A further equilibrium which must be taken into account is the decomposition of cyanide into cyanamide and carbon:

$$Ba(CN)_2 \rightleftharpoons BaNCN+C$$

This decomposition begins at about 500°C., and the equilibrium ratios of cyanide/cyanamide at temperatures from 500° to 900°C. have been measured by Franck and Neubner (Z. Elektrochem. 1934, **40**, 693), who find that only 3% decomposition of cyanide occurs at 900°C. According to Ewan and Napier, the presence of barium oxide in the melt has a disturbing effect on the equilibrium, so that the relative amounts of cyanide and cyanamide produced by the action of nitrogen on mixtures of barium oxide and carbon are very erratic. They do not consider that barium carbide can be an intermediate product, since the pressure of carbon monoxide present is always greater than the equilibrium partial pressure which they determined for the reaction

$$BaO+3C \rightleftharpoons BaC_2+CO.$$

Hempel (Ber. 1890, **23**, 3388) and Stähler (Ber. 1916, **49**, 2292) found that the formation of cyanide was greatly favoured by working under a nitrogen pressure of 60 atmospheres, Stähler obtaining a product containing 74% of barium cyanide with no cyanamide. Caro (Z. angew. Chem. 1910, **23**, 2405) studied the effect of adding calcium and barium fluorides to the melt at 1,100°C. and 1,200°C. In no case was the barium nitrogenated to a greater proportion than 50%.

At higher temperatures it appears that as much as 80% or more of the barium can be nitrogenated (Badische Anilin und Soda Fabrik, B.P. 2133 of 1907, 22039 of 1906; Kaiser, F.P. 454237, 1912 ; 454238, 1913). Ewan and Napier suggest that, at temperatures above 1,200°C. barium carbide may be an intermediate product, since by applying Nernst's theorem to their measurement of the carbide-forming reaction mentioned above, they were able to calculate that the equilibrium pressure of carbon monoxide at 1,500°C. is 100 mm., and at 1,700°C. is 1,026 mm. These figures suggest that the carbide could exist under the experimental conditions obtaining at these temperatures. In this connection it may be noted that Franck and Neubner (Z. Elektrochem. 1934, **40**, 693) noticed the formation of carbide, as well as cyanamide, on heating barium cyanide above 900°C.

3. *From Hydrocyanic Acid.*—It is difficult to prepare pure anhydrous barium cyanide from the aqueous solution which is obtained by neutralising baryta with hydrocyanic acid, owing to the ready hydrolysis of the salt. In the case of calcium cyanide, which is a technically valuable compound, the pure anhydrous salt can under no condition be prepared from aqueous solutions, the hydrolysis being assisted by the formation of the relatively insoluble calcium hydroxide. An impure technical anhydrous calcium cyanide may be made, however, by the interaction of calcium oxide and hydrocyanic acid, both in the anhydrous state. The Deuts. Gold-u.-Silber-Scheideanstalt describes, in G.P. 555223, 1929, the preparation of a powdered product containing more than 40% $Ca(CN)_2$ by treating powdered calcium oxide with boiling anhydrous HCN. The presence of 1–3% (by weight of the HCN) of an accelerator such as ammonia or water is recommended in order to minimise the loss of HCN by polymerisation. The reaction may also be effected in an inert medium such as diethyl ether, in which calcium cyanide is insoluble. Similar proposals have been made by the Roessler and Hasslacher Co. (U.S.P. 1909042, 1933; 1950879, 1934).

Franck and Freitag (Z. angew. Chem. 1926, **39**, 1430) describe a method of making calcium cyanide of 99% purity by the action of hydrocyanic acid on a solution of calcium in liquid ammonia, when hydrogen is evolved and a precipitate of the diammoniate,

$$Ca(CN)_2,2NH_3,$$

is produced. The same compound may also be obtained by the action of HCN on a solution of calcium nitrate in liquid ammonia. It is stable *in vacuo* at 100°C., but begins to lose ammonia at 150–160°C., and is completely free from it after 2 hours at 180°C. Similar data are given by Poindexter in U.S.P. 1596120, 1926; 1652874, 1927. A manufacturing process on these lines has been developed by the I.G. Farbenindustrie A.-G., and is described in B.P. 300349, 1927. A calcium compound such as the oxide or nitrate reacts with hydrocyanic acid and ammonia in the presence of water to give small crystals of the diammoniate, which are dried by washing with an organic liquid taking up water and are then decomposed by heating to give a product of the following analysis: $Ca(CN)_2$ 85–88%, $Ca(OH)_2$ 8–11%, $CaCO_3$ 1·0%, NH_3 0·5%, which is used in fumigation.

Another method of manufacture of calcium cyanide is described in Metzger's B.P. 261722, 1925, and in Ind. Eng. Chem. 1926, **18**, 161. Liquid hydrocyanic acid reacts with calcium carbide according to the equation

$$CaC_2+2HCN=Ca(CN)_2+C_2H_2.$$

The reaction is carried out by stirring powdered carbide with excess of the liquid to complete the reaction, distilling off the excess and leaving a finely divided buff powder of the approximate composition $Ca(CN)_2,2HCN$, from which the hydrocyanic acid may be easily removed by heating *in vacuo*. According to Franck and Freitag (*l.c.*), the product from commercial carbide contains not more than 55% $Ca(CN)_2$ with 25% HCN, and after removing the hydrocyanic acid leaves impure calcium cyanide containing 25–30% CN.

PROPERTIES OF THE ALKALINE EARTH CYANIDES. — **Barium cyanide.** Crystals of the dihydrate, $Ba(CN)_2,2H_2O$, may be prepared by adding hydrocyanic acid to baryta in theoretical quantities, and evaporating the concentrated solution *in vacuo* (Joannis, Ann. chim phys. 1882, [5], **26**, 484). The evaporation may be avoided by drying pure $Ba(OH)_2,8H_2O$, *in vacuo* at 100°C., and suspending the finely divided powder of anhydrous barium hydroxide in dry light petroleum to be treated with a small excess of dry hydrocyanic acid also mixed with light petroleum; the dihydrate then crystallises directly:

$$Ba(OH)_2+2HCN=Ba(CN)_2,2H_2O$$

The dihydrate is very deliquescent, but may be converted into the amorphous monohydrate by drying *in vacuo* over sulphuric acid, and the monohydrate in turn may be completely dehydrated by gradual heating to 100°C. *in vacuo*. Although barium cyanide is much more stable than the other alkaline earth cyanides, it is difficult to avoid some hydrolysis during the above dehydration, so that the product often contains some barium hydroxide, which can, however, be removed by shaking the solid with a small quantity of hydrocyanic acid and petroleum and redrying, giving a practically pure product. If methanol is used instead of petroleum in the above preparation, a compound, $Ba(CN)(OCH_3)+CH_3OH$ is obtained, which on heating loses first methanol and then dimethyl ether, leaving

$$BaO+Ba(CN)_2$$

(Drechsel, J. pr. Chem. 1880, [ii], **21**, 77).

Dry methods of preparation always yield mixtures of cyanide and cyanamide; for instance, by heating barium ferrocyanide above 500°C. or by the action of nitrogen on barium carbide the same product, containing about 60% of its nitrogen as cyanamide, is obtained. This is due to the equilibrium

$$Ba(CN)_2 \rightleftharpoons BaNCN+C,$$

which has been studied, as already mentioned, by Ewan and Napier (J.S.C.I. 1913, **32**, 467) and by Franck and Neubner (Z. Elektrochem. 1934, **40**, 693).

Barium cyanide is a colourless solid, melting at 600°C. approximately, at which temperature it is appreciably volatile. It is soluble in water to the extent of 80 g. per 100 g. of water at 14°C., and much less soluble in alcohol.

Calcium cyanide cannot be prepared in the wet way. An aqueous solution of lime in hydrocyanic acid decomposes almost completely on boiling, and on evaporation *in vacuo* gives a crystalline compound, $3CaO\cdot Ca(CN)_2,15H_2O$ (Joannis), which decomposes completely in a vacuum, leaving only lime. Dry reactions at high temperatures, on the other hand, yield only calcium cyanamide, for in the case of the calcium compounds the cyanide-cyanamide equilibrium is more in favour of the cyanamide.

Finely powdered calcium cyanide is rapidly hydrolysed by atmospheric moisture, with almost quantitative evolution of hydrocyanic acid:

$$Ca(CN)_2+2H_2O=Ca(OH)_2+2HCN$$

On account of this property it finds use as a fumigant, which is applied to the space to be fumigated by blowing the fine powder as a cloud with air from a hand-operated fan. The hydrolytic decomposition is completed in a few minutes.

Magnesium cyanide has not been prepared, but is known in the form of a diammoniate corresponding to the calcium compound. This compound was first obtained by Bergstrom (J. Amer. Chem. Soc. 1924, **46**, 1565) by treating a solution of mercuric cyanide in liquid ammonia with magnesium. Olberg obtained it by treating a saturated aqueous solution of magnesium nitrate or chloride (1 mol.) with 4–6 mols. of ammonia, and then with a large excess of liquid hydrocyanic acid (U.S.P. 1609038, 1926). The compound, which is readily soluble in water but not in hydrocyanic acid, is precipitated and washed with hydrocyanic acid and dried *in vacuo* at 40°C. for at least 30 minutes. B.P. 314242, 1928, recommends the use of ethanol instead of water in the preparation, since the compound is practically insoluble in this solvent and the use of a large excess of hydrocyanic acid is therefore avoided.

$Mg(CN)_2\cdot 2NH_3$ is more stable than the corresponding calcium compound, the ammonia being removed only by prolonged heating *in vacuo* above 250°C.

V. HYDROCYANIC ACID.

TECHNICAL METHODS OF PREPARATION.—1. *From Ferrocyanides.*—Ferrocyanides give hydrocyanic acid on treating with dilute sulphuric acid (Gattermann, Annalen, 1907, **357**, 318). Only one-half of the cyanide is thus recovered as HCN, however, owing to the formation of the relatively insoluble Everitt's salt:

$$2K_4Fe(CN)_6+3H_2SO_4 \\ =6HCN+K_2Fe_2(CN)_6+3K_2SO_4$$

Everitt's salt can be incompletely reconverted into soluble ferrocyanide by boiling with caustic soda (Erlenmeyer), the complete conversion requiring the assistance of simultaneous oxidation with air, when Fe_3O_4 or ferric hydroxide is precipitated instead of ferrous hydroxide (Grossmann, B.P. 36, *cf.* 4513, both of 1903). Dewrance and Williams (B.P. 28074 of 1908) obtain complete decomposition of alkali ferrocyanides by distilling them with acid in the presence of a small amount of cuprous chloride; the action is supposed to be due to the intermediate formation of cuprous ferrocyanide having the property, exceptional among ferrocyanides, of yielding the whole of its cyanogen as hydrocyanic acid on decomposition with boiling dilute sulphuric acid. The decomposition of complex iron cyanides with steam in the absence of acids is mentioned in F.P. 721762, 1931; rapid removal of the hydrocyanic acid from the reaction zone is necessary in order to avoid secondary decompositions.

2. *From Thiocyanates.*—The reduction of alkali thiocyanates with hydrogen, when a part of the cyanide produced appears as hydrocyanic acid, has already been mentioned. With barium and cuprous thiocyanates (Conroy, Heslop and Shores, J.S.C.I. 1901, **20**, 320) the principal nitrogenous product is hydrocyanic acid, and in the case of the cuprous salt, the reaction begins below 300°C. Rossiter, Crowther and Albright (B.P. 4403 and 6226 of 1901) mixed cuprous thiocyanate with finely divided copper and heated the mixture with hydrogen at temperatures rising from 150° to 650°C. Hydrocyanic acid was evolved and cuprous sulphide formed.

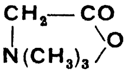
The most important method of converting thiocyanates into hydrocyanic acid is Raschen's nitric acid oxidation process (B.P. 10476, 10956, and 21678 of 1895; 19767 of 1898; 12180 of

1900), which has been operated on a commercial scale (Conroy, J.S.C.I. 1899, **18**, 432). A 15% sodium thiocyanate solution was allowed to flow into dilute nitric acid kept at the boiling-point by means of live steam:

$$NaCNS+2HNO_3=HCN+NaHSO_4+2NO$$

A slight excess of nitric acid was used in order to obtain a quantitative decomposition. The gases leaving the decomposer were scrubbed with a limited amount of water to remove traces of N_2O_3, the wash water being returned to the decomposer. The 33% of HCN in the resulting gas was actually removed by absorption in caustic soda solution of sp.gr. 1·37, avoiding the presence of an excess of hydrocyanic acid owing to its tendency to form polymerisation products in the presence of cyanide, and the cyanide solution evaporated to dryness *in vacuo*. A 96–99% yield of HCN is claimed. The nitric oxide remaining was mixed with air and the mixed gas scrubbed in flint-packed towers with water, giving a nitric acid solution of sp.gr. 1·12 which was returned to the system. Two more recent patents of the Gesellschaft für Kohlentechnik (B.P. 356190 and 356724, 1929) describe a similar process starting from ammonium thiocyanate, a readily available by-product from gas works.

3. *By the "Schlempe" Process.*—The juice of the sugar beet contains both inorganic and organic substances other than sugar, and these substances accumulate in the molasses. In Germany, the greater part of the molasses produced is treated with strontia, which combines with the sugar to form an insoluble sucrate. The liquid residue from this precipitate, which contains the impurities of the original juice in concentrated form, is known as "schlempe," and is concentrated to a sp.gr. of 1·4. It then contains 75% of dry substances, of which 30% are inorganic (mainly potassium) salts and the rest organic substances. It contains about 4% of nitrogen in the form of betaïne,



$$\begin{array}{l} CH_2\text{—}CO \\ |\qquad\quad \diagdown \\ \qquad\qquad\quad O \\ |\qquad\quad \diagup \\ N(CH_3)_3 \end{array}$$

and decomposition products of the vegetable proteins. A small part of the molasses which is not treated by the strontia process is fermented to alcohol, and the residue from this fermentation is known in France as "vinasses." When "vinasses" are distilled at 700–800°C. in horizontal iron retorts, vapours containing ammonia, the three methylamines, various higher alkylamines, methanol and combustible gases are evolved, and a solid mixture of potassium carbonate and carbon remains behind (Duvillier and Buisine, Ann. chim. phys. 1881, [5], **23**, 289; Ost, Z. angew. Chem. 1906, **19**, 609). Vincent worked this distillation process in 1877–1880 for the preparation of methylamines, and in 1879 Ortlieb and Müller developed a process for converting the methylamines into hydrocyanic acid, ammonia, methane and hydrogen by passing their vapours through a red-hot retort. This process was operated by the Société Anonyme de Croix (B.P. 3844 of 1879), the ammonia being absorbed in sulphuric acid and the hydrocyanic acid converted into ferrocyanide by treatment with a suspension of ferrous hydroxide in caustic potash. The manufacture of methylamines was abandoned in 1881 for want of a market, and with it the subsidiary production of cyanides.

The production of hydrocyanic acid from "schlempe" was put on to an economic basis by Bueb (*see* Reichardt and Bueb, B.P. 7171 of 1895; Bueb, B.P. 26259 of 1898), who cut out the intermediate separation of the methylamines and passed the "schlempe" distillation products directly to the cyanising furnace. Bueb's process (Muhlert, Chem. App. 1925, **12**, 156) is worked at the present time as follows: the liquid "schlempe" is run into a horizontal retort of the gas works type made of highly aluminous fireclay and heated by the residual gas formed in the process. The pasty carbonaceous residue has to be scraped out of the retort by hand, and is then lixiviated to recover potassium carbonate. The gases, after condensation of tar in a hydraulic main, pass directly to the cyanising chambers, which are filled with fire-brick checker-work. During the cyanising, which is carried out at above 1,000°C., carbon is deposited on the brickwork and the temperature falls; reheating is carried out by direct firing with producer gas, when the carbon deposit is burnt off. Two such chambers are therefore used alternately, one being reheated whilst the gases are being cyanised in the other. The cyanised gas contains 7% HCN, 7% NH_3, 8% hydrocarbons (mainly methane), 12% H_2, 18% CO, 24% CO_2, and 24% N_2. It is cooled and scrubbed with hot dilute sulphuric acid to remove ammonia. The hydrocyanic acid is then removed by water scrubbing in a 24-plate bubble cap column, a 2–3% aqueous HCN solution being obtained. This is distilled through a fractionating column having 11 plates. The hydrocyanic acid leaves the top of this column as a concentrated gas.

In the early days of the process, the hydrocyanic acid was worked up into ferrocyanide by the wet process for HCN-recovery from coal gas (*see* Ferrocyanides, p. 468). At the present time, however, it is converted into relatively pure briquetted sodium cyanide by the method described under Alkali Metal Cyanides, p. 481. Of the nitrogen in the "schlempe," about 45% is recovered as sodium cyanide, 20% as ammonium sulphate, and 35% is lost as elementary nitrogen.

The decomposition of monomethylamine at a red heat into hydrocyanic acid, ammonia, methane and hydrogen was noted by Wurtz (Ann. chim. phys. 1850, [iii], **30**, 443), who established the following equation:

$$3CH_3NH_2=2HCN+NH_3+CH_4+3H_2$$

The behaviour of di- and tri-methylamines under similar conditions, when passed through heated porcelain tubes containing broken porcelain, firebrick or charcoal, has been studied by Voerkelius (Dissertation, Hannover, 1909). The formation of hydrocyanic acid from dimethylamine begins at 600°C., and between 800° and

1,100°C. quantitative decomposition according to the equation

$$NH(CH_3)_2=HCN+CH_4+H_2$$

occurs. Increasing dilution of the dimethylamine vapour with hydrogen leads to the production of ammonia by the reaction

$$NH(CH_3)_2+2H_2=NH_3+2CH_4.$$

With a gas containing 50% hydrogen hardly any ammonia is formed, but with 97% hydrogen no hydrocyanic acid is produced. Similar results were obtained with trimethylamine, which at temperatures between 800° and 1,000°C. decomposes to the extent of 98% according to the equation

$$N(CH_3)_3=HCN+2CH_4,$$

and 2% according to

$$N(CH_3)_3+3H_2=NH_3+3CH_4.$$

Within the above temperature range, the results are not much affected by changes in the time of contact or the amount of heated surface exposed to the gas. But at higher temperatures, or in the presence of iron or refractory materials at longer times of contact, considerable decomposition of the hydrocyanic acid into its elements occurs. At 600°C. no decomposition of the trimethylamine occurred to give hydrocyanic acid, and at 720°C. the yield was only 78%.

The Deuts. Gold-u.-Silber-Scheideanstalt vorm. Roessler (F.P. 447725, 1911, and 448722, 1912) claim that, by passing the "schlempe" gases at high velocity through heated passages made of fused quartz or of Dinas brick without filling material (thus having the smallest possible contact surface), the whole of the nitrogen is obtained as ammonia or hydrocyanic acid. According to G.P. 420729, 1924, the salts of trimethylamine, betaîne and hexamethylenetetramine (especially the hydrochlorides) give hydrocyanic acid on heating in greater yield than is obtained from the free bases, betaîne hydrochloride giving 70–80% of the theoretical quantity of HCN as compared with 50–60% obtainable from betaîne itself.

4. *From Ammonia and Carbon Monoxide.*—The production of hydrocyanic acid from carbon monoxide and ammonia by heating them in the presence of spongy platinum was first noticed by Kuhlmann (Annalen, 1841, **38**, 62). Jackson and Laurie (J.C.S. 1905, **87**, 433), working with the dry gases, were unable to confirm this observation, their only products on sparking, treating by the silent electric discharge, or in the presence of a heated platinum wire being ammonium cyanate and hydrogen:

$$CO+2NH_3=NH_4CNO+H_2$$

Mailhe and de Godon (Bull. Soc. chim. 1920, [iv], **27**, 737) found that alumina catalysed the production of hydrocyanic acid at 400–420°C., a rapid reaction occurring at 550°C.:

$$CO+NH_3=HCN+H_2O$$

Many catalysts have since been proposed in the patent literature, the most important being thoria and alumina (Badische Anilin und Soda Fabrik, B.P. 220771, 224438, 1923; I.G. Farbenind. A.-G., B.P. 300369; Deuts. Gold-u.-Silber-Scheideanstalt vorm. Roessler, B.P. 207830, 223918, 1922; Bredig and Elöd, B.P. 229774, 229973, 1923; G.P. 522532; U.S.P. 1598707, 1926; 1634735, 1927; Frank and Caro, B.P. 282379, 1926; 301093, 1927; G.P. 611726).

Further information on the catalytic reaction is given in the technical literature by Bredig and Elöd (Z. Elektrochem. 1930, **36**, 1003; 1931, **37**, 2), who worked with alumina, ceria and thoria at 500°, 600°, and 700°C. and at reaction times of 1–12 seconds. With a gas containing 20 volumes of carbon monoxide and 1 of ammonia, a contact time of 1 second at 700°C. with alumina gave a 65% yield of hydrocyanic acid from the ammonia, and 14% of the ammonia was lost by decomposition; with a volume ratio of $10CO:1NH_3$ under the same conditions, the HCN yield was 48%. Fuchs and Verbeek (Ind. Eng. Chem. 1935, **27**, 410) describe the production of an active alumina catalyst, probably in the form of a gel, by precipitation of aluminium hydroxide from aluminium salt solutions and drying the precipitate under controlled conditions. With this catalyst at 590°C., a gas mixture of initial composition $9CO:1NH_3$ gave a 54% conversion of ammonia into hydrocyanic acid with a contact time of 1 second.

Yields of this magnitude are surprising in view of the ease with which the reverse reaction, the hydrolysis of hydrocyanic acid to ammonia and carbon monoxide, can be carried to completion by heating with steam and a catalyst such as broken brick, iron oxide or manganese dioxide (*see* Carpenter and Linder, J.S.C.I. 1905, **24**, 63). The explanation is probably to be found in the reduction of the partial pressure of steam by the operation of the water gas equilibrium,

$$CO+H_2O \rightleftharpoons CO_2+H_2,$$

for which the equilibrium constant

$$[CO][H_2O]/[CO_2][H_2]$$

at 600°C. is 0·35. Bredig and Elöd (Z. Elektrochem. 1930, **36**, 1003) find that the use of an excess of carbon monoxide produces a greater increase in the HCN yield than a corresponding excess of ammonia, which is in harmony with the above explanation. The reaction mechanism when ceria is used as the catalyst is discussed in Z. Elektrochem. 1931, **37**, 2.

The separation of the hydrocyanic acid from the reaction mixtures offers difficulties, since unchanged ammonia and carbon dioxide are present in the gas. Many of the methods described under Alkali Metal Cyanides, p. 480, are applicable, and in addition it has been proposed (1) to freeze out ammonium cyanide (G.P. 444504, 1922), (2) to treat the ammonia and carbon dioxide with calcium sulphate and water

$$CaSO_4+2NH_3+CO_2+H_2O =CaCO_3+(NH_4)_2SO_4$$

as in a technical method for the manufacture of ammonium sulphate (U.S.P. 1606767), and (3) to absorb the hydrocyanic acid in active charcoal or silica gel. An interesting adaptation of the reaction to the direct production of fused sodium cyanide has been proposed in B.P. 301565, 1927, and in U.S.P. 1955229, 1934; a mixture of ammonia and carbon monoxide is caused to react with sodium hydroxide, carbonate, sulphide or other salt at 580–650°C.

5. *From Formamide.*—Hydrocyanic acid can be obtained by the catalytic dehydration of formamide:

$$\mathrm{H{\cdot}CO{\cdot}NH_2 = HCN + H_2O}$$

Formamide itself may be prepared by the following methods:

(*a*) From formic acid and ammonia, which give ammonium formate. On distilling ammonium formate, water containing small quantities of ammonia and formic acid is first given off, and at 180°C. the distillation of formamide begins. As the temperature is raised to 220°C., increasing quantities of carbon monoxide are evolved. The reactions occurring are:

$$\mathrm{H{\cdot}CO{\cdot}ONH_4 \rightarrow H{\cdot}CO{\cdot}NH_2 + H_2O}$$

$$\mathrm{H{\cdot}CO{\cdot}ONH_4 \rightarrow H{\cdot}CO{\cdot}OH + NH_3}$$

$$\mathrm{\rightarrow H_2O + CO + NH_3}$$

Experiments on this decomposition are described by Lorin (Annalen, 1864, **132**, 255) and by Freer and Sherman (Amer. Chem. J. 1898, **20**, 223), who recommend that the dehydration be carried out in an atmosphere of ammonia. The use of dehydrating catalysts such as bauxite for the vapour phase reaction at 170°C. is protected by the Badische Anilin und Soda Fabrik in B.P. 237528, 1925).

(*b*) From alkyl formates and ammonia, the reaction having been discovered by A. W. Hofmann (J.C.S. 1863, **16**, 72), who saturated ethyl formate with ammonia and heated it in a sealed tube at 100°C. for 2 days. Alkyl formates are produced by treating solutions of sodium alkoxides in the corresponding alcohols with carbon monoxide under pressure (Stähler, Ber. 1914, **47**, 580):

$$\mathrm{CO + NaOMe = Na{\cdot}CO{\cdot}OMe}$$

$$\mathrm{HOMe + Na{\cdot}CO{\cdot}OMe = H{\cdot}CO{\cdot}OMe + NaOMe}$$

At the ordinary temperatures the reaction is slow, but goes to complete ester formation on prolonged treatment with carbon monoxide at 300 atmospheres; at 190°C., however, only 4% of the alkoxide reacts. Similar results were obtained by Fischer and Tropsch (Ges. Abh. Kennt. Kohle, 1921, **6**, 382), using sodium formate as catalyst, and by Christiansen (J.C.S. 1926, **129**, 418) on passing a mixture of carbon monoxide and methanol vapour over sodium methoxide at 70–100°C., high pressures and low temperatures favouring the formation of ester. According to B.P. 252848, 1925, when methanol containing 10 g. of dissolved sodium per litre is heated to 80°C. with carbon monoxide at 60 atmospheres, 75% of the alcohol is converted into methyl formate in 3 hours, whilst at 1,000 atmospheres the reaction is complete in a few minutes.

The manufacture of formamide by this reaction is described in B.P. 240087, 1925. Methyl formate is first made by dissolving sodium in methanol and treating the solution with carbon monoxide as above. The product is then treated with ammonia at 60°C. and 150 atmospheres. B.P. 254787, 1925, describes a vapour phase method by which methyl formate vapour is passed with ammonia over a dehydrating catalyst such as alumina, thoria or silica gel at 200–300°C. with a short time of contact: at higher temperatures or with longer contact times the principal product is hydrocyanic acid.

(*c*) From ammonia and carbon monoxide directly. K. H. Meyer and Orthner (Ber. 1921, **54**, [B], 1705) obtained some formamide, together with ammonium carbonate, formate, and cyanide, on heating a mixture of carbon monoxide and ammonia at 200°C. and 230 atmospheres in the presence of earthenware. A similar process is described in B.P. 203812, 1922, but is not of technical interest owing to the predominance of side reactions. The process described in B.P. 240087 above may be carried out by introducing the ammonia and carbon monoxide simultaneously into the sodium-methanol solution under the stated conditions, when it would fall under this head. The R. and H. Chem. Co. describe, in U.S.P. 1787483, a similar reaction at *e.g.* 70°C. and 17 atm.

The dehydration of formamide to yield hydrocyanic acid will obviously require temperatures higher than 200°C., since formamide itself is produced by dehydration of ammonium formate at that temperature. From thermochemical data it may be calculated that the reaction is endothermic, the equilibrium therefore favouring HCN-formation at high temperatures, and it proceeds with an increase in gas volume, so that the yields of hydrocyanic acid are greater at lower pressures. The variation of the equilibrium constant $k_p \left(=\frac{[\mathrm{HCN}][\mathrm{H_2O}]}{[\mathrm{H{\cdot}CO{\cdot}NH_2}]}\right)$ with temperature is given by the relation

$$\log k_p = -\frac{23380}{4{\cdot}571\mathrm{T}} + 1{\cdot}75 \log \mathrm{T} - \frac{0{\cdot}0046}{4{\cdot}571}\mathrm{T} + 3{\cdot}5,$$

the partial pressures of the components being expressed in atmospheres. From this relation, the percentage conversion of formamide to hydrocyanic acid at equilibrium at various temperatures and under total pressures of 1 and 0·02 atmospheres may be calculated as follows:

Temp. °C.	Percentage conversion.	
	1 atm.	0·02 atm.
200	8·8	53·1
300	25·0	87·7
350	—	97·3
400	77·8	99·4
500	96·7	—
600	99·4	—

Under favourable conditions the yields obtained in practice approximate to those calculated.

In the technical practice of this theoretically very favourable reaction for the production of hydrocyanic acid, several difficulties arise. It is found that liquid formamide near its boiling-point decomposes rapidly, though the vapour is relatively stable. For this reason it is necessary that the liquid be kept at its boiling-point for the shortest possible time, and the I.G. Farbenind. A.-G. propose to obtain vaporisation without decomposition by dropping the liquid (preferably under reduced pressure) on to a superheated surface kept considerably above 215°C., so that vaporisation is immediate and no liquid accumulates in the evaporator (B.P. 301974, 1927). Side reactions may occur during the dehydration, the most important being the reaction of hydrocyanic acid with steam to give carbon monoxide and ammonia. The use of catalysts which accelerate formamide dehydration but which do not favour the secondary decomposition is therefore of advantage. The most important catalysts are alumina, thoria and zirconia, especially after pre-heating to 1,000°C. to reduce their activity in promoting **HCN**-decomposition (B.P. 305816, 1928), and certain metals such as brass and steel (U.S.P. 1675366, 1928, and 1951520, 1934). The beneficial effect of working under reduced pressure (B.P. 269166, 1926, and 261557, 1925), or with formamide vapour diluted with ammonia (B.P. 233080, 1924), is also mentioned.

The last technical problem presented by this process is the supply of the heat quantities necessary to maintain the endothermic reaction at the high space velocities employed. Heat transfer is probably aided by the use of metallic tubes filled with metallic catalyst as reaction chambers (G.P. 477437, 1926), and Can. P. 285200, 1928, describes a reaction chamber having brass walls heated to a temperature above 300°C., no portion of the formamide being more than half an inch from the heated walls. A further method of obtaining rapid heat supply is to pass the vapour of formamide through a bath of fused metal heated to 300–600°C.; G.P. 561816, 1930, claims 70–85% yields of hydrocyanic acid by this method. Finally, it is claimed in B.P. 292749, 1927, that an alumina catalyst may be deposited on a wire gauze which can be heated electrically during the passage through it of formamide vapour.

6. *From Ammonia and Hydrocarbons.*—Hydrocyanic acid is produced by a large variety of gaseous reactions between ammonia and carbon compounds. Since the synthesis of **HCN** from its elements is highly endothermic, these reactions are generally favoured by high temperatures, and the reaction temperature required for **HCN** formation rises in passing from the most unsaturated hydrocarbon, acetylene, through ethylene to the completely saturated methane. With the unsaturated hydrocarbons, catalysts may usefully be employed to accelerate the cyanisation at temperatures between 500° and 900°C., but with methane very high temperatures are required (above 1,000°C.), and very short times of contact must be used in order to minimise loss by secondary decompositions. Equilibrium is never attained, and in general the use of catalysts is inadvisable, since under the severe conditions they are more likely to accelerate the unwanted side reactions than the cyanide synthesis. The following paragraphs give an account of the development of this method of cyanising ammonia, and of the modifications of and improvements in the simple reactions which have been proposed in order to overcome the technical difficulties involved.

(*a*) *Acetylene and Ammonia,* when passed over bauxite, hydrated ferric oxide, or the chlorides of zinc, iron, etc., at temperatures between 300° and 450°C., give condensation products such as acetonitrile (G.P. 387962, 1916), pyridine and its homologues (G.P. 382091, 1920), and the ethylamines (B.P. 283163, 1927). When metallic catalysts at higher temperatures are used, for example, copper in the form of a wire net at 480°C., hydrocyanic acid is the principal product if the acetylene is in large excess (Beindl, U.S.P. 1444457, 1915). Bredig, Elöd and Demme (Z. Elektrochem. 1930, **36**, 991) used a catalyst of pure alumina, and with equal volumes of acetylene and ammonia at 800°C. and contact times of 1–4 seconds they found 28% of the ammonia converted into hydrocyanic acid, 60% unchanged, and 12% decomposed. Much of the acetylene was decomposed into carbon or was polymerised. Using excess of ammonia, the acetylene could be fairly completely converted into hydrocyanic acid. According to Bredig, Elöd and Demme, the reaction is $C_2H_2+2NH_3=2HCN+3H_2$. The use of an alumina catalyst for the formation of hydrocyanic acid from ammonia and either acetylene or benzene is mentioned in G.P. 555056, 1927.

(*b*) *Ethylene and Ammonia* also react to give hydrocyanic acid, under conditions studied by Bredig, Elöd and Demme (*l.c.*). They found that precipitated alumina mixed with quartz was the best catalyst, which gave the following results at 800°C. with a gas mixture consisting of equal volumes of ethylene and ammonia :

Contact time seconds.	% ammonia unchanged.	% of disappearing NH_3	
		as HCN	as N_2
6·5	9·0	78·5	21·5
3·3	18·4	77·2	22·8
1·2	35·9	69·2	30·8
0·67	72·3	57·0	43·0

Considerable quantities of methane and carbon were also formed. The same catalyst was found effective by Elöd and Nedelmann (Z. Elektrochem. 1927, **33**, 217) for the reaction between ethylene and nitric oxide at 800–950°C. Probably the nitric oxide is first reduced to ammonia, which then reacts with the decomposition products of the ethylene ($C_2H_4=CH_2{:}+CH_2{:}$ and $CH_2{:}+NH_3=HCN+2H_2$). Using a gas mixture containing $1NO:2C_2H_4:2H_2$ at a temperature of 950°C. and a time of contact of 1·25 seconds, they obtained a 64·8% yield of hydrocyanic acid based on the nitric oxide, 2·4% appearing as ammonia. A large part of the ethylene yielded methane, carbon and hydrogen.

(c) *Methane and Ammonia* give very poor yields of hydrocyanic acid at temperatures up to 1,100°C. in the presence of alumina as a catalyst: this catalyst accelerates instead the decomposition of the methane and ammonia, as is shown by the following results (Bredig, Elöd and Demme, Z. Elektrochem. 1930, **36**, 991) with a mixture of equal volumes of the two gases:

Contact time seconds.	Temp. °C.	% NH_3 decomposed.	% NH_3 as HCN	% CH_4 decomposed.
8·8	800	56·5	trace	0·0
8·0	900	88·2	1·8	15·1
7·4	1000	98·5	9·0	47·6
6·8	1100	100	6·0	85·6

On the other hand, Bredig and Elöd claim better results in G.P. 548798, 1927, when using ethane instead of methane on a mixed alumina-silica catalyst at 850°C., a 35% yield of hydrocyanic acid being obtained. Probably acetylene is first formed.

Poindexter (U.S.P. 1584137, 1926) describes the production of hydrocyanic acid from ammonia and methane-containing gas (*e.g.* natural gas) at reaction temperatures between 950° and 1,450°C., depending on the materials of construction and the form of the apparatus. Preheating of the reactants is advisable in order that the contact time at reaction temperature may be kept as short as possible. 45–61% conversions of ammonia into hydrocyanic acid were obtained when 2 volumes of natural gas and 1 volume of ammonia were passed in 1 second or less through a glazed fireclay tube at 1,200°C. or higher. The loss of ammonia by decomposition was 27–39%. Various methods of supplying the necessary heat to support the reaction are described, such as the use of a chequer work stove preheated by combustion of fuel gas, or of a bed of coke which is blown red-hot by an air blast and then used as the reaction medium, or the addition to the gases of an insufficient quantity of oxygen for the combustion of their carbon, followed by explosion of the mixture. Further details are given in U.S.P. 1387170, 1920, and 1562914, 1922, according to the latter of which the product gas contains 11% HCN and considerable quantities of finely divided carbon.

The non-catalytic reaction between methane and ammonia is recommended by Wheeler and others (B.P. 335585, 335947, 1929), who find that the reaction

$$CH_4+NH_3=HCN+3H_2$$

proceeds at high velocities without the aid of solid surfaces if the temperature is of the order of 1,400°C., whereas the unwanted decompositions of methane and ammonia are catalysed by the walls of the chamber. They obtain good HCN efficiencies by choosing conditions which do not favour these decompositions, recommending, for example, the use of chambers with the smallest surface and the dilution of the gases with hydrogen and moisture (B.P. 353407, 1930). They also state that the decomposition of ammonia and methane is minimised by building the reaction chambers with refractories free from iron, and in such a way that the internal surfaces are smooth. In B.P. 349958, 1930, they describe a form of apparatus designed to facilitate the transfer of the heat required to maintain the reaction, consisting of reaction chambers of long, deep and narrow form placed between long and deep heating flues.

One further process may be mentioned here (Ruhrchemie A.-G., G.P. 630767) in which mixtures of ammonia and methane are heated to high temperatures (1,400–1,500°C.) in vessels of non-porous alumina refractory at reduced pressure and very low times of contact. These reaction conditions have previously been found to be favourable for the production of acetylene from methane, and the patent claims that, in the presence of ammonia, they lead also to the production of outstanding yields of hydrocyanic acid. A gas mixture containing 2 volumes of methane and 1 of ammonia gave, with a contact time of 0·05 second at a temperature of 1,500°C. and a pressure of 45 mm., an exit gas containing 12% HCN in amount corresponding to a 65% yield on ammonia and 32% on methane, with simultaneous production of acetylene. These results are in harmony with the view of H. Küster (Brennstoff-Chem. 1931, **12**, 329) that the first step in the synthesis of hydrocyanic acid from methane is the splitting up of CH_4 molecules into $CH\vdots$ groups.

The greatest technical difficulty in the methane-ammonia process is the rapid supply of heat at very high temperatures through refractory walls to the reacting gases, and various methods of overcoming it have been suggested. Peters and Küster (Brennstoff-Chem. 1931, **12**, 122) heated the gases at 20–40 mm. pressure by means of an electric discharge, and obtained good yields. With a mixture of ammonia and methane in the volume ratio of 1 : 7, for example, they report complete cyanisation of the ammonia, the excess methane being largely converted into acetylene. Wheeler also describes the production of hydrocyanic acid by passing induction sparks through a mixture of methane and ammonia (B.P. 325860, 1928), the power consumption being 0·05 kwh. per g. of HCN, or 0·01 kwh. per g. of HCN when the gas mixture is preheated to 1,000°C.

Another method of supplying internally a large part of the heat required is to add oxygen to the reacting gases, converting the endothermic synthesis

$$CH_4+NH_3=HCN+3H_2-60\text{ kg.-cal.},$$

into the exothermic oxidation reaction

$$NH_3+1\tfrac{1}{2}O_2+CH_4=HCN+3H_2O+114\cdot9\text{ kg.-cal.}$$

Such a process is described in B.P. 361004, 1931, and 451609, 1935, the combustible mixture being passed at a high speed through a platinum or platinum-iridium gauze catalyst at 950–1,100°C., and U.S.P. 2000134, 1935, describes the passage of the preheated mixture through finely divided wood charcoal at 1,100–1,500°C. L. Andrussov (Angew. Chem. 1935, **48**, 593) discusses the mechanism of the catalytic oxidation at a platinum gauze, and postulates the intermediate production of " nitroxyl " groups HNO by the oxidation of ammonia. In the presence of excess of oxygen (as in technical ammonia oxidation for nitric acid), " nitroxyl " is further oxidised to nitric oxide and water, but when methane is present the following reactions are said to occur :

$$HNO+H_2CH_2=HNCH_2+H_2O$$

$$HNCH_2=HCN+H_2$$

If methane is used in large excess, most of the oxygen is used in producing carbon monoxide and hydrogen, and the yield of hydrocyanic acid falls. The reactions by which " nitroxyl " and then hydrocyanic acid are formed are stated to occur very rapidly at the surface of the catalyst. At 1,000°C., using a methane-ammonia-air mixture in the proportions required for the above oxidation equation, 58–63% of the ammonia was converted into hydrocyanic acid, 8–12% into nitrogen, and 26–30% was undecomposed.

The reaction between nitric oxide and methane in the presence of alumina at high temperatures was mentioned by Elöd and Nedelmann (Z. Elektrochem. 1927, **33**, 217), and B.P. 446277 (Du Pont de Nemours and Co.) protects the use of one or more metals of the platinum group as catalysts for the reaction between hydrocarbons and nitric oxide, the mixture being diluted with nitrogen, carbon dioxide, steam or oxygen.

7. *From Nitrogen and Hydrocarbons.*—In 1868 Berthelot (Compt. rend. 1868, **67**, 1141) discovered that acetylene and nitrogen combine under the influence of strong induction sparks to give hydrocyanic acid by the reaction

$$C_2H_2+N_2 \rightleftharpoons 2HCN,$$

which is reversible. He had previously shown (Ann. chim. phys. 1863, [iii], **67**, 52) that acetylene is formed in the electric arc between carbon electrodes in an atmosphere of hydrogen, and that hydrocarbons in general yield acetylene under the influence of induction sparks. Acetylene is, in fact, one of the equilibrium products in the gas surrounding a carbon arc burning in hydrogen or hydrocarbon vapour, being present to the extent of 7–8% by volume, along with 1·25% methane, 0·75% ethane, and no other hydrocarbons (Bone and Jerdan, J.C.S. 1901, **79**, 1042). Berthelot drew the general conclusion that hydrocyanic acid must be formed in the carbon arc burning in mixtures of hydrogen and nitrogen, and when sparks are passed through mixtures of nitrogen and hydrocarbons. A mixture of 10 vols. of acetylene, 14·5 vols. of nitrogen, and 75·5 vols. of hydrogen is suitable for the synthesis of hydrocyanic acid, since mixtures richer in acetylene deposit carbon. The cyanogen compound observed when the arc burns between carbon electrodes in an atmosphere of nitrogen is hydrocyanic acid, the hydrogen being derived from the electrodes or from water vapour. Dewar (Proc. Roy. Soc. 1879, **29**, 188; 1880, **30**, 85) confirmed these results, and also showed that hydrocyanic acid is formed when a mixture of hydrogen and nitrogen is passed through a carbon tube heated externally by an electric arc. Hutton and Smith (B.P. 23835 of 1906; Trans. Amer. Electrochem. Soc. 1908, **13**, 358) have shown that the temperature of the arc is not necessary, hydrocyanic acid being formed when a carbon rod is heated at 1,700°C. in a mixture of hydrogen and nitrogen H. v. Wartenberg (Z. anorg. Chem. 1907, **52**, 299) carried out quantitative measurements of the equilibrium and obtained the following results with a mixture of equal volumes of hydrogen and nitrogen :

Temp. °C.	1635	1752	1875
% HCN in gas at equilibrium	1·95	3·10	4·70

Wallis (Annalen, 1906, **345**, 353) obtained a maximum HCN concentration of 35% with the same gas mixture in an arc having an estimated temperature of about 3,250°C. From acetylene mixed with twice its volume of nitrogen, Hoyermann (Chem.-Ztg. 1902, **26**, 70) obtained a 60–70% conversion into hydrocyanic acid on passing the mixture into the arc through tubular carbon electrodes.

Mixtures of acetylene and nitrogen under 3 atmospheres pressure were exploded in a closed bomb by Garner and Matsuno (J.C.S. 1921, **119**, 1903), and the cooled gases contained 1·57% HCN with an initial mixture containing 3% N_2, and 3·24% HCN with a mixture containing 22% N_2. The effect of increasing the temperature of the explosion by adding oxygen to the mixture was investigated by Garner and Saunders (J.C.S. 1924, **125**, 1634). The temperatures attained in the explosion varied from 2,950°C. to 4,287°C., but the quantity of hydrocyanic acid formed in the products corresponded with an equilibrium frozen at some lower temperature. Writing the reaction as

$$H_2+2C+N_2=2HCN-55{\cdot}4 \text{ kg.-cals.},$$

and using the relation

$$\log k_p = -\frac{13{,}210}{T}+0{\cdot}625\log T-0{\cdot}0009515T+\frac{1{\cdot}18T^2}{10^7}+3{\cdot}4,$$

where $k_p=[HCN]^2/[H_2][N_2]$, for the variation of the equilibrium with temperature, it was calculated that the temperatures at which equilibrium was frozen lay between 1,940° and 2,282°C.

A considerable amount of work has been done on the synthesis of hydrocyanic acid from nitrogen and methane (or its equivalent). Gruszkiewicz (Z. Elektrochem. 1903, **9**, 83) found that carbon monoxide, hydrogen and nitrogen, mixed in the volume ratio of 2 : 1 : 1, gave small amounts of hydrocyanic acid when exposed to induction sparks between platinum points. Lipinski (Z. Elektrochem. 1911, **17**, 761) passed mixtures of methane, nitrogen, and hydrogen through a 2,200-volt alternating current arc between platinum electrodes. No carbon was deposited from a mixture containing 20% CH_4, 10% H_2, and 70% N_2, and under the best conditions the HCN yield was 1·75 g. per kwh. According to H. Philipp (Chem. and Met. Eng. 1920, **22**, 313), Lipinski's process was tried on a commercial scale in 1914 at Neuhausen, and a yield of 30 g. HCN per kwh. attained. Briner and Baerfuss (Helv. Chim. Acta, 1919, **2**, 663) report a yield of 7·39 g. HCN per kwh. on circulating a mixture of 5 parts of nitrogen and 1 of methane through an arc at 505 volts between platinum electrodes 5 mm. apart.

A commercial process for the arc synthesis of hydrocyanic acid from methane and nitrogen has been developed by Soc. Chem. Ind. in Basle and H. Andriessens (B.P. 296355, 1927). Methane or petroleum vapour and nitrogen are circulated through an arc flame, producing a mixture of hydrocyanic acid and acetylene. The hydrocyanic acid is dissolved in caustic soda and worked up for sodium cyanide, and a large part of the acetylene is removed by solution in water under pressure before returning the gases to the arc (B.P. 195239). Küster (Brennstoff-Chem. 1931, **12**, 329) carried out arc experiments under reduced pressure, and at the highest energy input was able to convert 80·5% of the methane into hydrocyanic acid and 13·9% into acetylene, starting with a mixture containing 86·5% N_2 and 13% CH_4. With less nitrogen in the starting gas, the HCN/C_2H_2 ratio in the product fell. It is suggested that the methane is first decomposed into hydrogen and $CH:$ groups, which react with activated nitrogen. A large excess of nitrogen and a high energy input are necessary to make the concentration of active nitrogen sufficient to react with all the $CH:$ groups produced.

I.G. Farbenind. A.-G. (B.P. 294494, 1927) has devised various modifications of arcs of the Schönherr type to make them applicable to mixtures of hydrogen, nitrogen and hydrocarbons, obtaining a lengthening of the arc by interposing between the central electrode and the earthed tubular counter-electrode a mantle of insulating material which surrounds the arc and lengthens its path. From mixtures containing 7–30% CH_4, yields of 50–65 litres of acetylene and 15–18 g. HCN per kwh. are obtainable.

PROPERTIES OF HYDROCYANIC ACID.—Hydrocyanic acid does not occur in the free state in nature, but its compounds are widely distributed in plants. These compounds are glycosides which decompose, under the hydrolytic action of enzymes in the living cells, into hydrocyanic acid, a ketone or an aldehyde (*e.g.* acetone, benzaldehyde, etc.) and a sugar. For instance, the glucoside amygdalin, which is contained in bitter almonds, hydrolyses under the influence of the enzyme emulsin to give hydrocyanic acid, benzaldehyde and *d*-glucose; the hydrolysis is also effected by boiling with dilute acids. In rare cases a glycoside is found without an accompanying enzyme, as in the leaves of the common elder (*Sambucus nigra*) which contain the glucoside sambunigrin, isomeric with amygdalin (*v.* Cyanophoric glycosides). The quantity of hydrocyanic acid present varies in different parts of the same plant, and depends on the age of the plant, usually being greatest in young plants. It is also dependent on the conditions of growth as affected by climate and rainfall, and has been found to be increased by the use of nitrogenous fertilisers. The quantity present rarely exceeds 0·2% of the weight of the plant, and typical figures are given below:

Great millet (*Sorghum vulgare*), 0·013–0·044% in young plants; an exceptional North American specimen yielding 0·114%.

Wild cherry (*Prunus serotina*), 0·09%.

Cherry laurel (*Prunus Laurocerasus*), up to 0·2% in young leaves.

Cassava, sweet (*Manihot palmata*), 0·016% in leaves, 0·043% in peel of stem, 0·005% in edible part of root.

Cassava, bitter (*M. utilissima*), 0·041% in leaves, 0·113% in peel of stem, 0·053% in edible part of root.

Rangoon beans (*Phaseolus lunatus*), 0·025%.

Linseed (*Linum usitatissimum*), 0·02–0·038%.

Nandina domestica, 0·07–0·147%.

Bitter almonds (*Prunus communis*, var. *amara*), 0·12–0·18%.

Cases of cattle poisoning are not infrequent in hot countries where sorghum is used as fodder, and linseed meal and white clover are also sometimes poisonous. By thorough boiling with water the enzymes are destroyed and the cyanogenetic glucosides rendered harmless.

Minute traces of hydrocyanic acid have been observed in the products of incomplete combustion, such as the luminous flame of the Bunsen burner, boiler flue gases and tobacco smoke. Hydrocyanic acid is also always present in the products of the high-temperature dry distillation of nitrogenous organic substances, and in this case is probably chiefly formed by the action of ammonia on carbon:

$$NH_3+C=HCN+H_2$$

This reaction was used by Clouet (Ann. Chim. 1791, **11**, 30) in the first synthesis of hydrocyanic acid, and has been studied quantitatively by Bergmann (J. für Gasbeleuchtung, 1896, **39**, 117), Lance (Compt. rend. 1897, **124**, 819), Voerkelius (Dissertation, Hannover, 1909), Carpenter and Linder (Alkali Works, 45th Report, 1908, 26; 46th Report, 1909, 21), and Küster (Brennstoff-Chem. 1931, **12**, 329). The formation of hydrocyanic acid begins at 700°C., and the best yields (calculated on ammonia) are obtained between 1,000° and 1,100°C. The reaction is reversible, but equilibrium conditions are never reached owing to the simultaneous decompositions of ammonia and hydrocyanic acid at the temperatures in question. The composition of the product in any given experiment depends, therefore, on the relative rates of the main carbon-ammonia reaction and of the two decomposition reactions under the experimental conditions. Porcelain and iron, for example, favour HCN-decomposition, but little decomposition occurs with charcoal or when a layer of carbon has been deposited on the reaction tube. The rate of decomposition of the ammonia varies with the type of charcoal, being greater with more finely divided and with fresh samples of wood charcoal. Voerkelius found that the NH_3/HCN ratio in the product was not greatly influenced by the reaction time, but that ammonia decomposition increases with the reaction time. Küster's experiments imitated the conditions occurring in a coke oven, a mixture of nitrogen and hydrogen in the volume ratio of 1 : 3, and containing 0·2% of ammonia, being passed over coke. The results were:

Temp °C. .	600	700	800	900	1000	1100
% NH_3 giving HCN . .	3·7	5·2	5·4	12·8	25·1	40·0
% NH_3 decomposed . .	8·0	—	8·5	42·8	63·3	53·6

Nernst's heat theorem has been applied to this reaction by von Wartenberg (Z. anorg. Chem. 1907, **52**, 299) with the following results:

Temp. °C. . .	500	800	1100	1400
$[p_{NH_3}/(p_{H_2} \times p_{HCN})]$	632	0·27	0·003	0·0002

The equilibrium quantity of hydrocyanic acid increases markedly with rise of temperature, the heat of the endothermic reaction being −39,500 cal. per mol. of **HCN**. These figures indicate that equilibrium was never even approximately attained in Voerkelius' experiments, and the formation of appreciable quantities of hydrocyanic acid at 600°C. in Küster's experiments suggests that reactions between ammonia and hydrocarbons may contribute.

Hydrocyanic acid was formerly prepared by distilling potassium ferrocyanide with dilute sulphuric acid (*see under* Technical Methods of Preparation, p. 492), but is nowadays more conveniently prepared from sodium cyanide solution and relatively concentrated sulphuric acid, a method first described by Wade and Panting (J.C.S. 1898, **73**, 255). A 30–35% solution of sodium cyanide is run into hot 75% sulphuric acid, using 1½ mols. of sulphuric acid to 2 mols. of cyanide. The cyanide solution should be allowed to enter the acid just below its surface, in order to avoid contact of the alkaline cyanide solution with hydrocyanic acid vapour, which encourages polymerisation of the **HCN**. The vapour may be dried by means of calcium chloride at 30°C., and then condensed in an ice-cooled vessel. It may be purified from traces of water and ammonia by distillation over phosphorus pentoxide (Nef, Annalen, 1895, **287**, 265). Details of a similar laboratory procedure, adding a small amount of ferrous sulphate to the reaction mixture, are given by Slotta (Ber. 1934, **67**, [B], 1028).

The above process is frequently used for the manufacture of hydrocyanic acid (Pelton and Schwarz, Chem. and Met. Eng. 1919, **20**, 165; Carlisle, Ind. Eng. Chem. 1933, **25**, 959). The cyanide-sulphuric acid reaction mixture is distilled to give an aqueous distillate of 80% strength, which is acidified to inhibit decomposition, and rectified by redistillation. B.P. 401351, 1931, proposes the use of sulphur dioxide as a gaseous stabiliser to prevent decomposition throughout the reaction and distillation systems; it may conveniently be generated by adding sodium sulphite to the cyanide before the reaction with the acid.

Other methods of preparing hydrocyanic acid, which are of academic interest only, are (*a*) the dehydration of formaldoxime $CH_2{:}NOH$, an isomer of formamide obtained by the interaction of formaldehyde and hydroxylamine, on heating the two compounds alone or with phosphorus pentoxide (Dunstan and Bossi, J.C.S. 1898, **73**, 353), and (*b*) the combination of hydrogen and cyanogen by heating the mixture to 500–550°C. (Berthelot, Ann. chim. phys. 1879, [5], **18**, 380).

Hydrocyanic acid is a colourless liquid having a characteristic smell, or more correctly taste, which produces a choking sensation in the larynx. It is one of the most poisonous substances known; the fatal dose for a human being is approximately 1 mg. per kg. of body weight, or 0·06–0·07 g. for a full-grown man. It may be introduced into the body by inhalation of the vapour or by absorption of the liquid through the skin, and its lethal action is very rapid, large doses causing almost instantaneous death. On the other hand, air containing minute concentrations of the vapour, but in which its smell is distinctly perceptible, may be breathed constantly without ill effects. Experiments with cats, for instance, showed that concentrations of 0·003–0·004% could be tolerated, but that 0·005% produced symptoms of poisoning. It appears that the metabolism is able to convert hydrocyanic acid into relatively non-toxic thiocyanate at a limited rate, and if the rate of supply of hydrocyanic acid is lower than this rate, no lethal effect is produced. Thiocyanate has been detected in the urine of dogs which had been treated with regular small doses of potassium cyanide.

The first symptoms of poisoning are giddiness and darkening of the visual field; these symptoms disappear after a few minutes' exposure to fresh air. They are followed by unconsciousness accompanied by muscular cramps and more or less complete cessation of respiration. So long as the heart is still acting, however, artificial respiration and the use of oxygen (or a mixture of oxygen and carbon dioxide) may be successful at this stage in inducing recovery. Heart stimulants such as amyl nitrite (applied by inhalation of the vapour), lobeline, and coramine (applied by intravenous injection) may be applied by a doctor in desperate cases. Other antidotes which have recently been the subject of research are various sulphur-producing preparations, such as colloidal sulphur, thiosulphate, and tetrathionate, sodium nitrite and mixtures of nitrite with thiosulphate, methylene blue, and oxidising agents such as hydrogen peroxide and permanganate. When a cyanide has been swallowed, hydrocyanic acid is liberated in the stomach by the acids in the gastric juices, and in this case the simplest and most effective antidote is prepared by mixing solutions of ferrous sulphate and sodium carbonate. It is important that the sodium carbonate should be in excess so that the mixture is alkaline; the detoxifying action of this antidote is due to the conversion of the hydrocyanic acid into ferrocyanide, which is relatively non-toxic. A summarised description of the mode of action and relative efficiency of various antidotes for hydrocyanic acid poisoning is given by Wirth, Arch. exp. Path. Pharm. 1935, **179**, 558.

The poisonous action of hydrocyanic acid appears to consist partly of a direct paralysing effect on the respiratory nerve centres and partly of an inhibitory action on that enzyme of the red-blood corpuscles which brings about the transference of oxygen from oxyhæmoglobin to the oxidisable substances in the body: the venous blood therefore becomes arterial, and death is due partly to a kind of internal suffocation. The suggestion that the poisonous action of hydrocyanic acid might be due to its inhibitory action on the oxidising power of the blood was first made by Schönbein (J. pr. Chem. 1868, [i], **105**, 202), who showed that the acid inhibits the catalytic decomposition of hydrogen peroxide by plant ferments, and also by the red-blood corpuscles. Later Bredig and von Berneck (Z. physikal. Chem. 1899, **31**, 329) showed that it has the same effect on the inorganic catalyst, colloidal platinum. The ferments recover their activity when the hydrocyanic acid is removed. This property has been applied in the preservation of fruit.

The physical properties of liquid hydrocyanic acid are tabulated below:

Density (Fredenhagen and Dahmlos, Z. anorg. Chem. 1929, **179**, 77):

Temp. °C.	−13	0	4	15	20
Density	0·7326	0·7150	0·7096	0·6950	0·6884

Freezing-point (Tammann, Ann. Physik. 1899, **68**, 576):

Pressure (atm.)	1	500	4,000
Freezing-point (°C.)	−13·4	−2·88	+50·1

Vapour Pressure (Bredig and Teichmann, Z. Elektrochem. 1925, **31**, 449):

Temp. (°C.) . .	−15·2	−10	0	10·8
Vap. press. (mm.) .	110	165	256	427
Temp. (°C.) . .	14·8	18·0	25·6	29·8
Vap. press. (mm.) .	504	567	760	888
Temp. (°C.) . .	39·4	64·8	78·5	100
Vap. press. (atm.) .	1·63	3·71	5·35	9

Thermal Data.—Heat of formation of liquid from its elements (amorphous carbon) −21·8 cal. per mol. (Thomsen); (diamond) −24·8 cal. per mol. (Berthelot). Latent heat of vaporisation at 25°C., 246·8 cals. per g. (Perry and Porter, J. Amer. Chem. Soc. 1926, **48**, 299).

Heat of solution of liquid acid in water: according to Busay and Buignet, when 1 g.-mol. of liquid **HCN** is mixed with 1½ g.-mols. of water, a fall of temperature of 9·75°C. occurs.

Aqueous Solutions.—The specific gravities of aqueous solutions have been measured by Walker and Marvin (Ind. Eng. Chem. 1926, **18**, 139), whose results are given in an abbreviated form below:

Sp.gr.	0°	5°	10°	15°	20°	25°
0·682	—	—	—	—	—	100
0·690	—	—	—	—	99·8	97·7
0·700	—	—	—	99·0	96·9	94·8
0·710	—	—	98·1	96·0	93·9	92·0
0·720	99·3	97·2	95·1	93·0	91·0	89·1
0·730	96·2	94·2	92·0	90·0	88·0	86·2
0·740	93·1	91·1	89·0	87·0	85·1	83·3

These data are often used to estimate the percentage of water in the commercial acid.

The eutectic point, ice+solid **HCN**+liquid phase containing 74·5 molar percentage of **HCN**, is −23·4°C.

The dielectric constant of liquid hydrocyanic acid is 95, the largest known with the exception of that of hydrogen peroxide (Schlundt). The acid is miscible in all proportions with water, alcohol, ether, and many other substances, but it is almost insoluble in light petroleum. It is itself an excellent solvent for many solid substances; among inorganic salts the iodides are usually readily soluble. The solutions are good conductors of electricity, the conductivity of solutions of potassium iodide being about 3½ times greater than that of the corresponding aqueous solutions.

Hydrocyanic acid is one of the weakest acids, its dissociation constant in aqueous solution at 18°C. being $1{\cdot}3\times10^{-9}$, or 44 times smaller than that of sulphuretted hydrogen and 230 times smaller than that of carbonic acid (Walker and Cormack, J.C.S. 1900, **77**, 16). In a 0·1*N* solution, only 0·011% of the acid is ionically dissociated, so that it does not behave as an acid towards indicators, and its salts are very largely hydrolysed in aqueous solution. The hydrolysis of alkali cyanides has been studied by Harman and Worley (Trans. Faraday Soc. 1925, **20**, 502), who measured the dissociation constant $k=[\mathrm{KOH}][\mathrm{HCN}]/[\mathrm{KCN}]$ of the reaction $\mathrm{KCN}+\mathrm{H_2O} \rightleftharpoons \mathrm{KOH}+\mathrm{HCN}$ at various temperatures with the following results:

Temp. °C. .	5	18	25	35
$k\times10^4$.	0·179	0·229	0·254	0·304

The same figures apply to sodium cyanide. In the concentration of an aqueous cyanide solution free hydrocyanic acid produced by hydrolysis escapes until a sufficient excess of the base has accumulated to stop the hydrolysis: with stronger bases, such as caustic soda, the loss of hydrocyanic acid is slight, but with weaker bases it is considerable. In the case of volatile bases (*e.g.* ammonia) and insoluble bases (*e.g.* calcium hydroxide), the continued removal of the base from the solution (by volatilisation or precipitation) prevents the attainment of equilibrium, and nearly the whole of the hydrocyanic acid escapes. The carbon dioxide of the atmosphere will displace hydrocyanic acid from aqueous cyanide solutions, so that such solutions in confined spaces may develop dangerous **HCN** concentrations in the surrounding air.

Pure hydrocyanic acid, which has been dried over calcium chloride or distilled over phosphorus pentoxide, can be kept unchanged for long periods at the ordinary temperature. Instability is induced by heating the liquid to 100°C., or at the ordinary temperature by the presence of a small amount of water or of alkaline impurities such as ammonia or sodium cyanide, and the liquid gradually darkens in colour through yellow and brown, being finally converted into a non-volatile black solid of about the same empirical composition as **HCN** (Walker and Eldred, Ind. Eng. Chem. 1925, **17**, 1074). This black polymer is itself a catalyst for the polymerisation. The decomposition occasionally proceeds with explosive violence owing to the rapid rise of temperature which accompanies the reaction, and Salomone (Gazzetta, 1912, **42**, (i), 617) isolated from the products of an explosion colourless crystals of a substance having the composition of cyanic acid, the molecular weight of which in benzene solution corresponded to $(HCNO)_5$. From the solid black HCN polymer mentioned above, a termolecular polymer can be separated by extraction with ether (Nef), which is believed to be the nitrile of aminomalonic acid, $NH_2\cdot CH(CN)_2$, since it gives carbon dioxide, ammonia, and amino-acetic acid on heating with baryta water. From the same material, Bedel (Compt. rend. 1923, **176**, 168) obtained a tetramer which he believes to be the hydrocyanide of amino-methane dinitrile. The aqueous acid also becomes brown in the presence of alkali cyanides and deposits a dark brown amorphous substance, azulmin or azulmic acid, containing carbon, oxygen, nitrogen, and hydrogen in variable proportions. Whenever water is present, carbon monoxide and ammonia are found among the decomposition products. The discoloration of solid alkali cyanide on exposure to air is due to the hydrocyanic acid liberated at its surface undergoing the change to azulmic acid.

The commercial acid, which generally contains about 2% of water, is stabilised to inhibit decomposition by the addition of small quantities of strong acids, such as sulphuric acid or phosphoric acid, or better, oxalic acid, which is less corrosive to iron containers (G.P. 352979, 1919). Organic compounds which are readily hydrolysed to acid products are also suitable, *e.g.* cyanogen chloride (B.P. 258324, 1925), chloroformic esters (B.P. 254747, 1925).

The only useful application of hydrocyanic acid is in pest control, where its poisonous action is used against insects on growing plants and in various stored products, and against rodents and other pests in the fumigation of ships and mills, warehouses and other buildings, and in quarantine operations. This application was first developed by the Agricultural Experiment Station of the University of California for the fumigation of citrus trees (D. W. Coquillet and H. D. Bishop, California Station Bull. 122). The acid vapour is applied by erecting a tent over the tree and generating the acid inside it. The dosage applied must be high enough to kill the scale insects within about half an hour, but not high enough to cause damage to the foliage. Allowance must also be made for loss of fumigant by diffusion of the vapour through the tent during the period of exposure. Foliage is less liable to injury at night than in sunlight, and fumigation should not be carried out in damp conditions. The safe concentration of hydrocyanic acid depends on the kind of tree and on the time of the year. The minimum lethal dose varies widely for different species of pests, green aphis requiring only 2 g. of HCN per 1,000 cu. ft. of air space, and red spider up to 30 g. per 1,000 cu. ft. in greenhouse fumigation. The use of hydrocyanic acid in the fumigation of ships, warehouses and mills is now well established in many parts of the world, and is also extending to the treatment of stored products. In slum clearance schemes in England, hydrocyanic acid is being used for the eradication of vermin.

In early fumigation practice the hydrocyanic acid was generated *in situ* by the addition of solid sodium cyanide to a mixture of sulphuric acid and water, but since 1917 liquid hydrocyanic acid of about 98% strength has been marketed in tinned iron drums or steel cylinders (*see* Pelton and Schwarz, Chem. and Met. Eng. 1919, **20**, 165; Carlisle, Ind. Eng. Chem. 1933, **25**, 959; U.S.P. 1352665, 1355384, 1444300, 1569171, 1680662). For convenience in application the acid may be absorbed in granules of kieselguhr previously freed from alkaline impurities (B.P. 271236, 1926), or in discs of wood pulp. As already mentioned under Calcium Cyanide, p. 492, powdered calcium cyanide may also be used in a moist atmosphere for the generation of hydrocyanic acid.

Hydrocyanic acid readily forms addition products; for instance, with hydrochloric acid in ethyl acetate solution it gives the compound $2HCN\cdot 3HCl$, which has been shown to be dichloromethylformamidine hydrochloride,

$$HN{:}CH\cdot NH\cdot CHCl_2,HCl.$$

This compound decomposes at 100°C. into hydrochloric acid and a volatile substance $2HCN\cdot HCl$, which is chloromethylene formamidine, $HN{:}CH\cdot N{:}CHCl$. The latter compound is also formed when dichloromethylformamidine hydrochloride is treated with excess of liquid hydrocyanic acid at 40°C. When warmed with quinoline, chloromethylene formamidine gives a quantitative yield of iminoformyl *iso*cyanide $HN{:}CH\cdot NC$, a dimer of hydrocyanic acid (Hinkel and Dunn, J.C.S. 1930, 1834), which is a white solid melting at 85°C. Hinkel, Ayling and Beynon (*ibid.* 1935, 674) have investigated the hydrolysis of this compound with cold water to give ammonium formate, and its formation of insoluble complex compounds with silver nitrate, mercuric chloride and aluminium chloride. Hydrocyanic acid itself forms a compound with aluminium chloride, having the composition $AlCl_3\cdot 2HCN$ (Hinkel and Dunn, *ibid.* 1931, 3343), which is stated to be identical with the aluminium chloride compound of the dimer. The compound is unstable in moist air, and slowly evolves hydrocyanic acid *in vacuo* or on heating to 100°C.

Hydrocyanic acid is often used for the synthesis of α-hydroxy-acids from aldehydes and ketones, with which it combines under the influence of alkaline catalysts to give cyanhydrins, which are the nitriles of α-hydroxy-acids, *e.g.*:

$$\underset{\text{Acetaldehyde}}{CH_3CHO}+HCN \rightarrow \underset{\text{Acetaldehyde cyanhydrin}}{CH_3\cdot CH(OH)(CN)}$$

$$\rightarrow \underset{\text{Lactic acid}}{CH_3\cdot CH(OH)COOH}$$

It is also used for the synthesis of aromatic aldehydes by Gattermann's reaction.

Constitution of Hydrocyanic Acid.—The constitution of hydrocyanic acid is a very complex question, and cannot be said to have been definitely settled. The behaviour of its metallic salts would lead to contradictory conclusions: potassium cyanide reacts with esters to give nitriles $\mathrm{R\cdot C\vdots N}$ as principal product, whereas silver cyanide yields carbylamines or isocyanides $\mathrm{R\cdot N:C}$. The force of this evidence is in any case considerably reduced by the fact that in neither case is the one product exclusively formed. Other properties point to a difference in structure between the alkali cyanides and those of the heavy metals; for instance, silver and mercuric cyanides cannot be oxidised by permanganate, whereas potassium cyanide gives cyanate. On the other hand, it should be remembered that the heavy metal cyanides are scarcely ionised at all and their reactions are therefore those of the undissociated molecules; the alkali cyanides, on the other hand, are very largely ionised, and their reactions are those of the ions. For this reason it may be concluded that all metallic cyanides have the same constitution, and the generally accepted one is the *iso*nitrile configuration $\mathrm{M\cdot N:C}$. This agrees with their ready formation of stable addition compounds, in which they resemble the *iso*nitriles and differ from the nitriles.

Hydrocyanic acid itself may be tautomeric, $\mathrm{H\cdot N:C \rightleftharpoons H\cdot C\vdots N}$, but the weight of evidence in this case supports the nitrile formula as being at any rate greatly predominating. Like the nitriles, hydrocyanic acid is hardly affected by dilute mineral acids, from which it may be distilled unchanged; the carbylamines or *iso*nitriles, on the other hand, are violently decomposed. With alkalis, hydrocyanic acid is readily hydrolysed or decomposed, but even boiling alkalis are without action on *iso*cyanides Its high dielectric constant and marked solvent and dissociating powers relate it to the nitriles rather than to the carbylamines (Wade, J.C.S. 1902, **81**, 1613). Wade is also of the opinion that its physiological properties lend support to its configuration as a nitrile, but Nef draws the opposite conclusion. Anhydrous hydrocyanic acid and the nitriles do not dissolve silver cyanide, whereas the *iso*cyanides dissolve it readily.

VI. CYANOGEN AND ITS DERIVATIVES.

Cyanogen, $(\mathrm{CN})_2$, is prepared by heating dry mercuric cyanide at a dull red heat, the reaction by which Gay-Lussac discovered it in 1815:

$$\mathrm{Hg(CN)_2 = Hg + (CN)_2}$$

It may also be prepared by the interaction of sodium cyanide and copper sulphate, when the first product is a complex cupricyanide, $\mathrm{NaCu(CN)_3}$, which decomposes on heating to give cuprous cyanide, $\mathrm{Cu_2(CN)_2}$, and cyanogen. A further yield of cyanogen may be obtained by treating the cuprous cyanide precipitate with ferric chloride solution of sp.gr. 1·26:

$$\mathrm{Cu_2(CN)_2 + 2FeCl_3 = (CN)_2 + Cu_2Cl_2 + 2FeCl_2}$$

By all these methods a part of the cyanogen is always polymerised to dark brown, non-volatile paracyanogen. Paracyanogen appears to be the stable form at ordinary temperatures, but at high temperatures is converted into cyanogen. The velocity of the change is very small at temperatures below 300°C., so that cyanogen gas can be kept without change in the cold. The polymerisation of cyanogen, and the catalytic effect of glass, quartz, potassium cyanide, and sodamide have been studied by Perret and Krawczynski (Bull. Soc. chim. 1932, [iv] **51**, 622).

The direct synthesis of cyanogen from its elements is not of practical importance but has theoretical interest in relation to several technical cyanide syntheses. Cyanogen is formed when the electric arc burns between pure carbon electrodes in an atmosphere of nitrogen, though it cannot be detected in the gaseous product withdrawn from the arc (Wallis, Annalen, 1906, **345**, 353). Nernst's heat theorem would indicate that considerable quantities of cyanogen exist in equilibrium with carbon and nitrogen at the temperature of the arc:

Temp. (°C.) .	2,000	2,500	3,000	3,250
$\%(\mathrm{CN})_2$ in gas at equilibrium .	0·01	0·9	17·0	45·0

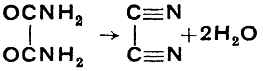
and von Wartenberg (Z. anorg. Chem. 1907, **52**, 299) observed a very intense cyanogen spectrum in the arc gases, and found that carbon is deposited at some distance from the arc. Cyanogen is therefore essentially unstable at temperatures below 2,500°C., and can only be preserved at much lower temperatures on account of its slow rate of decomposition. It can be detonated by means of mercury fulminate, and on heating its rate of decomposition becomes measurable at 1,200°C. (Berthelot, "Force des Matières Explosives," Paris, 1883, p. 113). It may be concluded from these figures that the direct union of carbon and nitrogen to cyanogen can play no part in the formation of cyanides by processes operated at ordinary furnace temperatures. On the other hand, it should be mentioned that cyanogen is said to be produced when nitrogen is passed over iron covered with coke at 1,500–1,800°C., and Belg. P. 378694, 1931, protects such a process, in which nitrogen at 50 atmospheres is heated in the presence of reduced iron with compressed carbon monoxide. Presumably there is intermediate formation of iron carbide and iron nitride.

Cyanogen is a very poisonous gas which burns with a characteristic peach-blossom-coloured flame. The liquid has a density of 0·89 at 13·8°C., boils at −20·7°C. at 1 atmosphere, and freezes at −34·4°C. Its vapour pressure at −22·9° is 701·6 mm., and at −14·4° is 1030·4 mm. (Cook and Robinson, J.C.S. 1935, 1001). The critical temperature and pressure are 128·3°C. and 59·6 atmospheres respectively (Cardoso and Baume, Compt. rend. 1910, **151**, 141). Water dissolves 4·95 volumes of the gas at 0°C. At 18°C. and higher the dissolved cyanogen is hydrolysed to hydrocyanic acid and cyanic acid, the latter being further hydrolysed to give carbon dioxide and ammonia (Naumann, Z. Elektrochem. 1910, **16**, 772). After some time the solution deposits dark brown azulmic acid, and contains also oxalic acid and urea. Cyanogen dissolves in caustic alkalis to give cyanide and cyanate by a reaction analogous to those of the halogens:

$$(CN)_2+2NaOH=NaCN+NaCNO+H_2O$$

Silver nitrate solution has no action on cyanogen which may be separated from a mixture with hydrocyanic acid by passing through silver nitrate solution to remove the **HCN**, and may be estimated by treatment with caustic soda and titrating the cyanide formed (Wallis, Annalen, 1906, **345**, 353).

Cyanogen is held to have the nitrile structure $N\colon C{-}C\colon N$, and not the *iso*nitrile structure $C\colon N{-}N\colon C$ or a mixed structure $N\colon C{-}N\colon C$, because of its formation by the dehydration of ammonium oxalate or oxamide with phosphorus pentoxide:



$$\begin{array}{c}OCNH_2\\|\\OCNH_2\end{array}\rightarrow\begin{array}{c}C\equiv N\\|\\C\equiv N\end{array}+2H_2O$$

which shows that the two carbons are linked together.

Cyanogen chloride, CNCl, is prepared by the action of chlorine on various metallic cyanides. Heavy metal cyanides, such as mercuric (Serullas, 1827) and zinc (Held, 1897) may be used, but the use of aqueous hydrocyanic acid, discovered by Berthollet in 1787, is now a preferred method. Alkali cyanides are not suitable because they react violently with cyanogen chloride in any but cold and very dilute solutions, giving dark brown amorphous products. U.S.P. 1938324, 1933, however, describes the production of cyanogen chloride from chlorine and sodium cyanide in a mixture of carbon tetrachloride and glacial acetic acid in the absence of water. For the preparation from aqueous hydrocyanic acid (Price and Green, J.S.C.I. 1920, **39**, 98T), a 12–15% solution of pure hydrocyanic acid is treated with a stream of finely divided chlorine bubbles, obtained by injecting the gas through a porous earthenware plate at about 40°C. The cyanogen chloride distils off as it is formed together with 10–20% of hydrocyanic acid. It is purified by retreatment with chlorine, or by shaking with zinc oxide to remove the hydrocyanic acid almost completely as zinc cyanide. Hydrochloric acid in the product is removed by distilling the liquid over sodium bicarbonate. A technical process for the preparation from aqueous hydrocyanic acid and chlorine under pressure is described in B.P. 347989, 1929.

Cyanogen chloride is a colourless liquid of density 1·193 at 14°C. (Cook and Robinson, J.C.S. 1935, 1001), which solidifies at −8°C. Its vapour pressure at various temperatures was measured by Regnault:

Temp. (°C.) . .	−30	−20	−10	0
Vap. press. (mm.) .	68·3	148·2	270·5	441·1
Temp. (°C.) . .	10	20	30	40
Vap. press. (mm.) .	681·9	1001·9	1427·4	1988·0
Temp. (°C.) . .	50	60	70	
Vap. press. (mm.) .	2719·3	3664·2	4873·2	

Its boiling-point at 760 mm. is 12·66°C. The vapour, which is very poisonous, attacks the eyes violently. It is slightly soluble in water, the cold saturated solution containing 6% of **CNCl**. The heat of formation of the liquid from its elements is −26·9 cal. per mol. It is stable for an indefinite period when pure, but in the presence of hydrochloric acid it polymerises to cyanuric chloride, $C_3N_3Cl_3$. Aqueous hydrochloric acid (stronger than 2*N*) hydrolyses it thus:

$$CNCl+2H_2O=NH_4Cl+CO_2$$

Its behaviour towards alkalis is the same as that of cyanogen bromide (*see below*), and indicates that cyanogen chloride is the acid chloride of cyanic acid, **CNOH**. Hydriodic acid hardly attacks it in the cold, and it is without action on iron and copper in the cold.

Cyanogen bromide, CNBr, may be prepared by the action of bromine on a metallic cyanide or on hydrocyanic acid. Slotta (Ber. 1934, **67**, [B], 1028) gives details of the action of sodium cyanide solution on bromine in a well-stirred flask immersed in a freezing-mixture, the bromocyanogen being distilled direct from the reaction mixture through a layer of calcium chloride into a cooled receiver. A laboratory preparation is also described in "Organic Syntheses," **1931, 11,** 30). The compound is of technical importance because its addition to a cyanide solution causes more rapid dissolution of gold (Sulman and Teed, B.P. 18592 of 1894; J.S.C.I. 1897, **16**, 961). It is used in the treatment of a few refractory ores, especially those in which the gold is associated with tellurides, as in Western Australia. For this purpose it is always manufactured at the place of use by the action of acidified bromide-bromate solution on a concentrated solution of sodium cyanide; other oxidising agents may be used instead of bromate. Since the action of bromine on sodium cyanide also produces sodium bromide, the addition of a further quantity of bromate will yield a further supply of bromine and hence of cyanogen bromide; with an adequate quantity of bromate, therefore, the reaction is (Göpner, Z. angew. Chem. 1901, **14**, 355):

$$2NaBr+NaBrO_3+3NaCN+3H_2SO_4 \\ =3Na_2SO_4+3CNBr+3H_2O$$

The reaction occurring when gold dissolves in bromocyanide solution is as follows:

$$2Au+3NaCN+BrCN \\ =2NaAu(CN)_2+NaBr$$

Its effect is thus seen to be due to its character as being both a cyanide compound and an oxidising agent (*see* Gold Cyanides, p. 486).

Cyanogen bromide is a colourless, crystalline substance melting at 52°C. and boiling at 61°C. Its solubility in water is about 5–6% at the ordinary temperature. It is very poisonous, and has an intensely irritating effect on the mucous membrane and the eyes. Like cyanogen chloride, the pure substance can be kept without change, but traces of bromine or of hydrobromic acid cause its rapid polymerisation to cyanuric bromide, $C_3N_3Br_3$, with simultaneous partial decomposition. It is very slowly hydrolysed by water to hydrobromic and cyanic acids:

$$CNBr+H_2O=HCNO+HBr,$$

the cyanic acid being next hydrolysed to ammonia and carbon dioxide. These reactions occur instantaneously with caustic alkalis, much more slowly with alkali carbonates, and not at all with bicarbonates. In connection with the bromo-cyanide process of gold extraction, it is of interest to note that cyanogen bromide slowly reacts with potassium cyanide in aqueous solution, giving cyanogen:

$$CNBr + KCN = (CN)_2 + KBr$$

A 0·1–0·2% **CNBr** solution is completely decomposed in 3–6 hours by **KCN** solution of less than 1% strength.

In aqueous solution, cyanogen bromide acts as an oxidising agent, converting hydriodic acid into iodine, and sulphuretted hydrogen into sulphur:

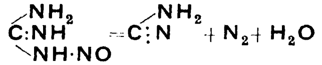
$$CNBr + 2HI = HCN + HBr + I_2$$
$$CNBr + H_2S = HCN + HBr + S$$

In these reactions the bromine behaves like hypobromous acid, which is typical of bromine attached to nitrogen (Chattaway and Wadmore, J.C.S. 1902, **81**, 191), so that the compound must be formulated as an *iso*-cyanogen derivative, **C:N·Br**. The reaction with potassium iodide provides a convenient method for the quantitative estimation of cyanogen bromide.

Cyanamide, $NH_2{\cdot}CN$, is obtained by the action of ammonia on an ethereal solution of cyanogen chloride (Cloëz and Cannizzaro, Compt. rend. 1851, **32**, 62), when ammonium chloride crystallises out and cyanamide is recovered from the ethereal solution by evaporation. It is also obtained by the action of mercuric oxide on thiourea:

$$CS(NH_2)_2 + HgO = NH_2{\cdot}CN + HgS + H_2O$$

Several guanidine derivatives yield cyanamide on boiling with water or alkalis; for example, nitroso-guanidine decomposes thus (Thiele, Annalen, 1893, **273**, 136):



$$C{:}NH\begin{matrix}\diagup NH_2\\ \\ \diagdown NH{\cdot}NO\end{matrix} = C{\vdots}N\begin{matrix}\diagup NH_2\\ \\ \end{matrix} + N_2 + H_2O$$

Cyanamide is most easily prepared from its metallic salts. Disodium cyanamide, **Na_2NCN**, is formed by the action of sodamide on carbon or on sodium cyanide (*see* Alkali Metal Cyanides, p. 480), or by passing carbon dioxide over heated sodamide (Geuther, Annalen, 1858, **108**, 93):

$$NaNH_2 + CO_2 = NH_2{\cdot}COONa$$
$$= NaCNO + H_2O$$
$$NaCNO + H_2NNa = Na_2N{\cdot}CN + H_2O$$

It is also formed when either sodium cyanate or sodium cyanide is fused with sodium hydroxide, or when ammonia reacts with sodium carbonate at 500–700°C. (G.P. 582625, 1928). The calcium and barium salts are produced by the nitrogenation of the carbides (*see under* Alkaline Earth Cyanides, p. 487). and by several other reactions at moderate temperatures where cyanide would be expected, *e.g.* from lime and hydrocyanic acid (Franck and Bank, Z. anorg. Chem. 1933, **215**, 415) and by heating the ferrocyanides. They are also formed by heating the carbamates or the cyanates to redness (Drechsel, J. pr. Chem. 1877, [ii], **16**, 188; 1880, [ii], **21**, 77) (*see also* G.P. 591039, 1929):

$$Ca(OCONH_2)_2 = CaN{\cdot}CN + 2H_2O + CO_2$$

and $$Ca(OCN)_2 = CaN{\cdot}CN + CO_2$$

Cyanamide is easily prepared from the disodium salt by neutralising its cold, aqueous solution with nitric acid and evaporating to dryness in a vacuum; the dry residue is extracted with ether. According to Liebknecht (Angew. Chem. 1932, **45**, 584; G.P. 601465, 1934), it is best to treat the disodium compound first with absolute alcohol to produce the mono-sodium salt and sodium ethoxide, and then to treat the mono-sodium salt with hydrogen chloride in ether solution. Werner (J.C.S 1916, **109**, 1325) describes its preparation from the readily accessible calcium salt: 100 g. are mixed with 125 g. of acetic acid and 120 g. of water, the mixture well kneaded and left for 24 hours, after which the friable mass is powdered and extracted with ether in a Soxhlet apparatus. The yield is 94–96% of the theoretical.

Cyanamide forms colourless, deliquescent crystals melting at 43–44°C. (Colson, J.C.S. 1917, **111**, 555). It is readily soluble in water, alcohol and ether, and sparingly soluble in carbon bisulphide, benzene and chloroform. On heating it polymerises very readily to dicyanodiamide, **$H_2N(C{:}NH)NH{\cdot}CN$**, a liquid which boils at 140°C. under 19 mm. with decomposition to melamine. Pinck and Hetherington (Ind. Eng. Chem. 1935, **27**, 834) produce the dimer in 98% yield from concentrated cyanamide solutions on heating with small amounts of ammonia. The neutral aqueous solution is stable, but polymerisation occurs in the presence of either acids or alkalis. The physico-chemical aspect of the process has been studied by Morrell and Burgen (J.C.S. 1914, **105**, 576) and by Grube and Krüger (Z. physikal. Chem. 1914, **86**, 65), who find that in alkaline solution the reaction takes place between undissociated cyanamide molecules and cyanamide ions:

$$H_2CN_2 + HCN_2' = H_3C_2N_4'$$

Hence the rate of polymerisation is at a maximum in a solution containing one-half of its cyanamide in the ionised form, which is virtually the case when one-half equivalent of a strong base is added to the aqueous solution. Weak bases, since their cyanamide salts are considerably hydrolysed, have a much smaller polymerising action than strong ones.

The action of acids on cyanamide causes polymerisation and hydrolysis (to urea) simultaneously. Cyanamide treated with 10–20% sulphuric acid at the ordinary temperatures is almost wholly converted into urea, whereas near the boiling-point polymerisation predominates (Carlson, Z. angew. Chem. 1914, **27**, 724). The reaction is further complicated by the hydrolysis of the dicyanodiamide to dicyanodiamidine,

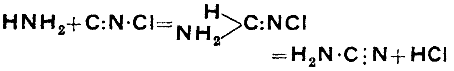
$$H_2N(C{:}NH)NH{\cdot}CN + H_2O$$
$$= H_2N(C{:}NH)NH{\cdot}CO{\cdot}NH_2,$$

a strong base which neutralises the acid.

Cyanamide readily forms addition compounds. For example, when dry hydrogen chloride is passed into a dry ethereal solution, a white crystalline substance having the formula $H_2CN_2{\cdot}2HCl$ is formed (Mulder and Smit, Ber. 1874, 7, 1634).

Cyanamide is an extremely weak acid, the first dissociation constant ($H_2CN_2 \rightleftharpoons H^+ + HCN_2'$) being of the order of 10^{-11} (Grube and Krüger, Z. physikal. Chem. 1914, **86**, 65). The monosodium salt, $NaHCN_2$, crystallises from a solution of cyanamide in absolute alcohol when sodium ethoxide is added (Liebknecht, Angew. Chem. 1932, **45**, 584); the disodium salt can only be prepared by one of the dry fusion methods mentioned above. The calcium salt, $Ca(HCN_2)_2$, can be obtained in solution by decomposing ordinary calcium cyanamide with water. The silver salt, Ag_2CN_2, is obtained as a canary-yellow precipitate by adding silver nitrate solution to a dilute ammoniacal solution of cyanamide; it is soluble in cold, dilute nitric acid. The lead salt is an orange-yellow precipitate.

Although there is some doubt as to the constitution of cyanamide ($H_2N{\cdot}C \vdots N$ or $H_2N{\cdot}N{:}C$), the balance of evidence is in favour of the normal cyanide structure, for cyanamide shows many reactions of a normal cyanide or nitrile, *e.g.* reaction with water to give the acid amide urea, with sulphuretted hydrogen to give thiourea, and with ammonia to give the amidine guanidine, $HN{:}C(NH_2)_2$. Its formation from cyanogen chloride, to which the *iso*nitrile structure is assigned, can be explained by the intermediate formation of an additive compound (Nef):



$$HNH_2 + C{:}N{\cdot}Cl = {}^{H}_{NH_2}\!\!>C{:}NCl = H_2N{\cdot}C \vdots N + HCl$$

VII. CYANATES.

The cyanates, salts of the acid $HCNO$, are not themselves of technical importance, but derive interest from their close relationship to the cyanides, from which they are readily formed by oxidation, and into which they are converted by reduction. This behaviour is held to support the "*iso*cyanide" structure for the metallic cyanides, since the oxidation to cyanate is then represented as a transition from divalent to tetravalent carbon:

$$Na{\cdot}N{:}C \rightarrow Na{\cdot}N{:}C{:}O$$

In the case of organic derivatives of cyanic acid, two series of compounds should exist, the normal cyanates $R{\cdot}O{\cdot}C \vdots N$, and the *iso*cyanates $R{\cdot}N{:}C{:}O$. Only the latter have been isolated, however, as the normal cyanates are so unstable that they polymerise to trimeric cyanurates as soon as they are formed.

Several reactions in which cyanates are formed have already been described, and need only be briefly mentioned here. Cyanates are formed by the action of alkalis on cyanogen (p. 503), or on cyanogen bromide (p. 504), and by the oxidation of cyanides on heating in air (p. 485). Ammonium cyanate is produced under certain conditions by reaction between carbon monoxide and ammonia (p. 494). An interesting synthesis of cyanic acid is described by Laude (Compt. rend. 1932, **194**, 2070), who oxidises carbon compounds with potassium permanganate in concentrated ammonia solution, using copper powder as a catalyst. By using the oxidising medium in large excess, he obtained good yields of cyanic acid from methanol (34 g. per 100 g.), methyl iodide (22 g.), and pinene (16 g.), and even greater yields from more complex acids and their derivatives.

The production of cyanates by the reaction of carbon dioxide and ammonia with alkalis such as caustic soda, sodium carbonate, or even sodium sulphide is frequently mentioned in the recent patent literature. The pressure synthesis of urea from carbon dioxide and ammonia,

$$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O,$$

is now an established technical process, and from the tautomeric relationship of urea to ammonium cyanate,

$$CO(NH_2)_2 \rightleftharpoons NH_4CNO,$$

it is not surprising that, if the synthesis is carried out in the presence of alkalis at suitable temperatures, alkali cyanates result. Such a process is described in B.P. 359559, 1930, the working conditions being 50 atmospheres pressure and a temperature of 400°C. H. Wittek (B.P. 358745, 1930) protects the reaction between ammonia-carbon dioxide mixtures and alkali oxides in the presence of catalysts such as copper, manganese, alumina, and charcoal, and in F.P. 731167, 1932, a beneficial effect is claimed for the addition to the reaction mixture of substances which will diminish or prevent the presence of water (which is formed in the reaction), such as carbon monoxide which reacts with it by the water gas reaction. The reaction temperature is generally between 500° and 800°C. The technical interest in these processes lies in the possibility of their being utilised as a step towards cyanide production; in B.P. 359559, for example, it is stated that cyanide results if the reaction product is subsequently heated with hydrogen, and in B.P. 358745 the addition of carbon to the solid raw material is proposed for the same purpose.

Cyanic acid, $HCNO$, is prepared by heating its polymer cyanuric acid, $H_3C_3N_3O_3$, which is itself obtained by the action of water on cyanuric bromide, $C_3N_3Br_3$, the triple polymer of cyanogen bromide (p. 504). It may also be prepared by warming urea with phosphorus pentoxide (Weltzien, Annalen, 1858, **107**, 219), and condensing the evolved vapour at −18°C. It is a volatile liquid, having a smell resembling that of strong acetic acid. It is extremely unstable and changes rapidly, even at 0°C., into the white amorphous polymeric substance cyamelide. Above 0°C. the change is explosively violent, and cyanuric acid is also formed. The solution in dry ether is comparatively stable, but if a small amount of triethyl phosphine is added, the triple polymer cyanuric acid is formed. The relationship between cyanic acid, $HCNO$, cyanuric acid, $(HCNO)_3$, and cyamelide, $(HCNO)_x$, where x probably equals 3, has been studied by Troost and Hautefeuille (Compt. rend. 1868, **67**, 1340) and by van't Hoff and van Deventer ("Studies in Chem. Dynamics," 1896). All of these substances yield the same vapour: at 150°C. and 50 mm. there is a triple point at which the two solid phases cyamelide and cyanuric acid co-exist together with the vapour phase. Above 150°C. cyanuric acid is the stable solid phase, and below 150°C. cyamelide. Cyanic acid is quite unstable (having a higher vapour pressure at the same temperature) with respect to cyamelide.

The aqueous solution of cyanic acid is very unstable, rapid hydrolysis to ammonia and carbon dioxide occurring on warming:

$$HCNO+H_2O=NH_3+CO_2$$

Ammonium cyanate, NH_4CNO, is prepared as a white snow by mixing the vapour of cyanic acid, well diluted with an inert gas, and gaseous ammonia. On warming the solid, or its aqueous solution, ammonium cyanate is converted into urea: $NH_4CNO=CO(NH_2)_2$. The reversibility of the conversion and its equilibrium in aqueous solution have been investigated by Walker and Hambly (J.C.S. 1895, **67**, 746); at 100°C., in *N*/10 solution, 5% of the cyanate remains unconverted at equilibrium, and the equilibrium is little affected by temperature.

According to B.P. 354604, 1930, ammonium cyanate may be used as a starting point for the preparation of the cyanates of the metals of the first two groups of the periodic table, by treating it in alcoholic solution or liquid ammonia solution at 30–35°C. with the appropriate metallic oxide or hydroxide.

Potassium cyanate, $KCNO$, is readily prepared by grinding together dry potassium cyanide and the theoretical quantity of lead oxide, and heating the mixture to the melting-point of lead:

$$KCN+PbO=KCNO+Pb$$

The salt is recrystallised from water or dilute alcohol. J. Milbauer (Z. anorg. Chem. 1904, **42**, 433) observed the conversion of thiocyanate into cyanate by the agency of lead oxide at 300°C.:

$$KCNS+PbO=KCNO+PbS$$

The oxidation of cyanide may also be carried out electrolytically, by electrolysing a solution containing 4–6 mols. of KCN and 1 mol. of KOH per litre at 4–6 volts, and a current density of 1–4 amps. per square decimetre of anode surface, agitating the liquor at the anode (Paternò and Pannain, Gazzetta, 1904, **34**, (ii), 152). The oxidation is almost quantitative.

Potassium cyanate crystallises in thin transparent plates of sp.gr. 2·05, readily soluble in water and anhydrous ammonia, insoluble in absolute alcohol. It is fusible below red heat without decomposition.

Sodium cyanate, $NaCNO$, may be prepared by similar methods to those described under potassium cyanate. Its solubility in water is 10·68 g. per 100 g. of water at 16°C. It fuses without decomposition at about 500°C.

Lead cyanate is a crystalline precipitate formed when solutions of a lead salt and a soluble cyanate are mixed. The dry salt is stable, but hydrolyses on boiling with water into urea and lead carbonate.

Silver cyanate is slightly soluble in cold water (0·006 g. per 100 c.c. at 12°C.), but much more soluble in hot water. It is readily soluble in aqueous ammonia, and sparingly soluble in cold dilute nitric acid.

VIII. THIOCYANATES.

The thiocyanates or sulphocyanides, the sulphur analogues of the cyanates, are not in great demand in commerce, and the fact that some synthetic processes for their manufacture have at times excited technical interest is due to the possibility of converting them into the valuable cyanides (*see* Alkali Metal Cyanides, p. 480). The commercial requirements of thiocyanates are at present completely satisfied by the gas works production, and this source could easily be expanded to meet any possible increase in the demand.

TECHNICAL METHODS OF PREPARATION.—1. *From Ammonia and Carbon Disulphide.* This synthesis was first brought into practical operation by Gelis (B.P. 1816 of 1860; *see also* Hofmann, Reports Juries, Intern. Exhib. of London 1862, 59). A concentrated solution of ammonia and ammonium sulphide was agitated with carbon disulphide, yielding a solution of ammonium thiocarbonate,

$$(NH_4)_2S+CS_2=(NH_4)_2CS_3,$$

which was then heated to 90–100°C. with potassium sulphide:

$$2(NH_4)_2CS_3+K_2S \\ =2KCNS+2NH_4SH+3H_2S$$

Günzberg and Tcherniac (B.P. 1148 of 1878, 1359 of 1879, 1261 of 1881) avoided the troublesome formation of large quantities of sulphuretted hydrogen by heating 20% ammonia solution with carbon disulphide at 100°C. under pressure in stirred vessels. The reaction in this case is (Conroy, J.S.C.I. 1896, **15**, 8):

$$4NH_3+CS_2=NH_4CNS+(NH_4)_2S$$

The formation of ammonium sulphide increases the ammonia consumption and is responsible for the pressure developed during the reaction. Crowther and Rossiter (B.P. 17846 of 1893), and Brock, Hetherington, Hurter and Raschen (B.P. 21451 of 1893) overcame both drawbacks by adding lime to the charge, when calcium thiocyanate and hydrosulphide are formed:

$$2NH_3+2CS_2+2Ca(OH)_2 \\ =Ca(CNS)_2+Ca(SH)_2+4H_2O$$

To avoid the formation of calcium thiocarbonate, the reaction must be carried out in the presence of an excess of ammonia, which is afterwards distilled off. The residual mixture is treated with carbon dioxide to remove sulphuretted hydrogen and to precipitate the equivalent calcium carbonate, and the clear solution of calcium thiocyanate used for the preparation of the thiocyanates of other metals.

2. *From Cyanamide and Sulphur.*—A process is disclosed in B.P. 384662, 1931, and 412254, 1932, for preparing thiourea by heating technical calcium cyanamide with sulphur or substances containing sulphur, or with sulphides, at temperatures up to 150°C., and then heating the reaction mixture to about 250°C., when the thiourea is converted into thiocyanate and ammonia. If salts of the alkali metals are present, *e.g.* potassium sulphate, a solution of potassium thiocyanate can be obtained by leaching the reaction product. The temperature at which cyanamide can be converted into thiocyanate is thus much lower than that at which it can be converted into cyanide (*see* Alkaline Earth Cyanides, p. 488), but considering the thiocyanate process as a step in a cyanide synthesis, it is doubtful whether this advantage of lower working temperatures can compensate for the further complications involved in converting the thiocyanate into cyanide (*see* Alkali Metal Cyanides, p. 480).

3. *From Coal Distillation Gases.*—Coal distillation gases are at present the sole source of thiocyanates, which are found in spent oxide from gas purification, and also in gas liquor and ammonia still effluent.

Spent Oxide may contain 0–10% of ammonium thiocyanate, depending on the composition of the gas being purified and on the conditions under which the oxide mass has been regenerated (rapid action with consequent rise of temperature favours thiocyanate formation). The whole of the cyanogen contained in the spent oxide can be recovered as calcium thiocyanate by heating with milk of lime under pressure above 100°C. (Marasse, G.P. 28137), when the iron cyanide compounds and the free sulphur in the mass react to give calcium ferrocyanide and calcium sulphite, which then react together with more sulphur to give calcium thiocyanate and calcium sulphate; the iron appears as ferrous sulphide. According to Hölbling (Z. angew. Chem. 1897, **10**, 162, 297) the reaction is only 70% complete, but the conversion is improved by using baryta or barium sulphide instead of lime, when a mixture of barium thiocyanate and barium thiosulphate is produced.

Gas Liquor is virtually a very dilute solution of thiocyanate, as is shown by the following figures relating to Linder's analyses of five English gas liquors (Chief Inspector of Alkali Works, 42nd Rep., 1905, 35):

Analysis in g./litre.

Sample.	1	2	3	4	5
HCN as ferrocyanide .	0·068	0·0	0·576	0·460	0·0
HCN as thiocyanate .	1·688	4·457	1·238	1·029	1·042
HCN as hydrocyanic acid .	0·680	0·0	0·030	0·050	0·355

The formation of ammonium thiocyanate in gas liquor is due to the action of dissolved air on the ammonium sulphide in the fresh liquor, giving ammonium polysulphides which react with the ammonium cyanide present to give thiocyanate:

$$(NH_4)_2S_2 + NH_4CN = NH_4CNS + (NH_4)_2S$$

Owing to its great dilution and its alkalinity (due to ammonia), this solution is unsuitable for the economic recovery of thiocyanate. The liquor is instead distilled in ammonia stills, and the gases (ammonia, carbon dioxide, sulphuretted hydrogen and some hydrocyanic acid) evolved are passed into sulphuric acid for the production of ammonium sulphate. The waste liquor from the stills contains about 0·15% of thiocyanate in the form of the calcium salt, which is best recovered as the cuprous salt by treating the acidified liquor with copper sulphate and a reducing agent such as sulphur dioxide (Parker and Robinson, B.P. 2383 of 1889), or by treating the liquor (after removing excess of calcium hydroxide with carbon dioxide) with freshly precipitated cuprous oxide (B.P. 11964 of 1893).

Formation of Thiocyanate directly from Coal Gas.—The hydrocyanic acid present in coal gas can be quantitatively fixed as thiocyanate under suitable conditions. The necessary sulphur for the reaction can be provided by scrubbing the gas with a sodium polysulphide solution (Marriott, B.P. 3311 of 1877), or with a suspension of manganese dioxide in water, which produces sulphur by oxidising sulphuretted hydrogen in the gas (Campbell and Boyd, B.P. 10186 of 1888). H. Wood Smith, Gidden, Salamon and Albright (B.P. 13653 of 1901) proposed simply to scrub the gas with an aqueous suspension of sulphur, obtaining a solution containing up to 200 g. of ammonium thiocyanate per litre. This process is in operation at several gas works. In the process described by A. E. Broadberry (J. Gas Lighting, 1912, 31; B.P. 23624 of 1909) the sulphur is provided by spent oxide, which is charged into an ordinary purifier box and continually sprayed with water to keep it moist, while the gases pass upwards through it. The reactions are:

$$H_2S + 2NH_3 + S = (NH_4)_2S_2$$

$$(NH_4)_2S_2 + HCN + NH_3 = (NH_4)_2S + NH_4CNS$$

In order to prevent water-logging, the direction of the gas flow is changed at intervals, and the spent oxide charge is removed after 6–8 weeks. The capacity of a 20 ft. by 20 ft. purifier box containing a 2 ft. layer of spent oxide is $3·5 \times 10^6$ cu. ft. of gas per day, and 3–5 lb. of ammonium thiocyanate are obtained per ton of coal, in the form of a 26% solution.

Properties of the Thiocyanates.—**Ammonium thiocyanate, NH_4CNS,** crystallises in anhydrous, colourless leaflets of sp.gr. 1·3 and melting-point 159°C. 100 g. of water dissolve 122 g. of the salt at 0°C. and 162 g. at 20°C. It is readily soluble in alcohol. The fused salt above its melting-point is partly converted into the isomeric thiourea. At 220°C., decomposition into the volatile products ammonia, sulphuretted hydrogen and carbon bisulphide occurs, and guanidine thiocyanate remains behind.

Potassium thiocyanate, $KCNS$, crystallises in anhydrous, striated prisms or needles of sp.gr. 1·9 and melting-point 172·3°C. It is deliquescent and very soluble in water :

Temp. (°C.)	0	20	25
Solubility (g./100 g.)	177·2	217	239

It is also soluble in anhydrous ammonia, and in various organic liquids as follows :

Solubilities (g./100 g. of solvent).

Acetone	20·8 at 22°		20·4 at 58°
Ethyl acetate	0·44 at 0°	0·4 at 14°	0·2 at 79°
Amyl alcohol	0·18 at 13°		2·14 at 100°
Pyridine	6·75 at 0°	4·97 at 58°	3·21 at 115°

The fused salt becomes deep blue at 430°C., probably due to the liberation of sulphur.

Thiocyanogen, $(CNS)_2$, is obtained by the action of a solution of a halogen in an anhydrous solvent on a metallic thiocyanate ; for instance, from a dry ethereal solution of bromine cooled to 0°C. and lead thiocyanate. On cooling an approximately $N/2$ solution of thiocyanogen in carbon bisulphide to −70°C., almost colourless crystals melting at −3° to −2°C. are obtained, which decompose at the ordinary temperature. The chemical behaviour of thiocyanogen is similar to that of the halogens: its electronegative character is at least equal to that of iodine. The molecule is believed to contain two thiocyanogen radicles, and to have the constitution $N \vdots C \cdot S \cdot S \cdot C \vdots N$ (Söderback, Annalen, 1919, **419**, 217). A standard solution is used for determining the thiocyanogen values of fats ; with compounds containing one double bond they resemble the iodine numbers, but only one double bond in linoleic acid is attacked. The method has been used for finding the composition of natural oils (Freudenberg, Arch. Pharm. 1925, **263**, 675 ; Z. Unters Lebensm. 1926, **51**, 15).

Uses of Thiocyanates.—Thiocyanates do not find large-scale application in technical industry, the annual world output being estimated at 150 tons (Chem. Trade J. 1936, **98**, 434). The aluminium and tin salts have been used in the dyeing and printing industry to a small extent, and the yellow compound canarin, (*q.v.*) obtained by oxidising potassium thiocyanate with a strong oxidising agent such as chlorate and hydrochloric acid, has been used as a yellow dye for wool. Ammonium thiocyanate is used as a fixing agent in photography.

Thiocyanates are plant poisons, and their use (especially in the form of the ammonium salt) as weed-killers has been proposed (*see* Chem. Trade J. 1936, **98**, 498). Frankland and Silvester (J.S.C.I. 1907, **26**, 231) investigated the germicidal properties of thiocyanates. They found that goldfish were not affected in 24 hours by concentrations of up to 260 parts per 100,000 of thiocyanate in the form of the potassium salt, but that as little as 10 parts per 100,000 were sufficient to control *Bacillus coli communis*. Thiocyanates are present in the animal organism, in the human saliva, gastric juice, conjunctiva secretion and urine.

Organic thiocyanates have been proposed as insecticides (U.S.P. 1841458, 1932 ; Murphy and Peet, J. Econ. Entomol. 1932, **25**, 123; Hartzell and Wilcoxon, B. 1936, 612).

Analytical.

The methods of analysis described here are those commonly employed in technical laboratories. For further details, an analytical textbook or a work on technical analysis should be consulted.

The Detection of Cyanide Compounds is based chiefly on two characteristic, deeply coloured cyanide derivatives, namely Prussian blue and the red ferric thiocyanate. The Prussian blue reaction is given directly by ferrocyanides when their neutral or acid solutions are treated with ferric salt solutions, a blue precipitate or a blue coloration due to ferric ferrocyanide being produced. The reaction may be applied to simple cyanide solutions (after evaporating them down to small bulk with a little alkali if they are very dilute) by treating them with ferrous sulphate solution to form ferrocyanide, and then producing Prussian blue by adding ferric salt solution, or better by adding an oxidising agent such as nitric acid to convert the excess of ferrous salt into ferric salt, with the same result. The latter procedure is stated to give quicker precipitation of Prussian blue, and greater sensitivity (Vorländer, Ber. 1913, **46**, 181). Verhoever and Johns (J. Amer. Chem. Soc. 1915, **37**, 601) give details of a method of this kind. The dilute cyanide solution is evaporated, after the addition of a little sodium hydroxide, *in vacuo* at a temperature below 70°C. to a volume of 1 ml., 0·2 ml. of 3% $FeSO_4$ and 0·05 g. of KF are added, and after 10 minutes a small excess of 30% HNO_3. The blue colour is compared wth that produced by a known quantity of KCN under similar conditions. For a similar method Kolthoff (Z. anal. Chem. 1919, **57**, 1) claims a sensitivity of 2 mg. CN per litre.

A deep red coloration due to ferric thiocyanate is produced when a ferric salt is added to a neutral or acid thiocyanate solution. In the case of very dilute solutions, it is advantageous to shake the treated solution with a small quantity of ether to extract the ferric thiocyanate from the water. This test can be applied to cyanides by converting them into thiocyanates by means of ammonium polysulphide solution and can be made quantitative by matching the coloration produced with that of a standard thiocyanate solution. Johnson's method (J. Amer. Chem. Soc. 1916, **38**, 1230) is as follows: an HCN solution containing 0·1–8 mg. of HCN is made alkaline with KOH, treated with 1 ml. of ammonium polysulphide solution, and evaporated to dryness ; the residue is extracted with acetone, which dissolves only the $KCNS$, and the acetone removed by evaporation ; the residue is dissolved in water and treated with 2 ml. of 0·5% $FeCl_3$, the colour being matched by means of a standard thiocyanate solution. Castiglioni (Gazzetta, 1933, **63**, 171) treats the aqueous cyanide solution with sulphur dissolved in acetone and claims a sensitivity of 1 in 50,000.

Another sensitive colour test for cyanides is the sodium picrate test, which gives a reddish-violet coloration depending on the formation of sodium *iso*purpurate when the cyanide is in excess, and of amino-nitrophenols when picrate is in excess (A. C. Chapman, Analyst, 1910, **35**, 469). The liquid to be tested is mixed with an equal volume of a solution containing 0·05% picric acid and 0·5% Na_2CO_3, and digested at 40°C. for 1 hour. The colour is compared with that produced by a standard HCN solution, and the sensitivity is 1 part of HCN in 500,000 of water (Waller, Proc. Roy. Soc. 1910, **82**, B, 574).

Several colour tests have been proposed for the detection of minute concentrations of HCN in the atmosphere of ships and buildings after fumigation. In the benzidine-copper acetate test (Pertusi and Gastaldi, Chem.-Ztg. 1913, **37**, 609; Hamer, J. Roy. Sanit. Inst. 1933, **53**, 563), the cyanogen formed by the action of HCN on cupric acetate oxidises benzidine to a blue substance. The test is carried out by dipping a filter paper into a mixture of equal volumes of a 0·3% solution of copper acetate and a 0·1% solution of benzidine acetate, draining surplus solution from the paper and introducing the damp paper into the atmosphere to be tested. HCN concentrations of 0·002% and higher are readily detected, a blue coloration being developed in 10 seconds, but the rapid action makes it difficult to estimate the actual concentration. In the mercuric chloride test, the action of HCN on $HgCl_2$ to give non-ionised $Hg(CN)_2$ and HCl is detected by having present an indicator with a well-marked colour change in the appropriate p_H range, *e.g.* methyl orange (Sherrard, Public Health Reports, Reprint No. 1224, 1928, Treasury Dept., U.S. Public Health Service). The methyl orange-mercuric chloride test is much slower than the benzidine copper acetate test, and is therefore better adapted to the estimation of actual HCN concentrations.

Cyanates are best characterised by the deep blue potassium cobalt cyanate, obtained by adding potassium and cobalt salt solutions to the cyanate solution made acid with acetic acid. Cyanide must be removed before the cobalt solution is added.

The nitroprussides give a deep violet coloration with alkali sulphides. The colour is obscured if heavy metals which form dark-coloured sulphides have not been previously removed from the solution.

Analysis of Alkali Cyanides.—Sodium and potassium cyanides are hygroscopic when cold, so that care is necessary in taking samples for analysis. The samples should be transferred immediately and without touching them with the hands to a hot iron mortar, coarsely crushed, and transferred to a well dried hot bottle, preferably fitted with a lightly greased glass stopper. Errors due to absorption of moisture in sampling occur very easily, and may be more serious than inaccuracies in testing.

The Estimation of Cyanogen is carried out by a modified Liebig's method. 5 g. of the sample are weighed out and made up to 500 ml., and 25 ml. of this solution, diluted to 200–300 ml., are titrated with pure silver nitrate solution until a faint turbidity is visible. The reaction is

$$2NaCN+AgNO_3=NaNO_3+NaAg(CN)_2,$$

and when this is completed, the further addition of silver nitrate leads to the precipitation of silver cyanide, thus:

$$NaAg(CN)_2+AgNO_3=NaNO_3+2AgCN$$

The silver nitrate solution must be neutral and free from lead and zinc. It is standardised by means of a solution of pure sodium chloride (dried by heating to redness before weighing), using pure potassium chromate as indicator. In impure solutions of cyanides, the end point is more easily observed if a little caustic soda and a few drops of 10% KI solution are added before running in the silver nitrate solution. Wellings (Analyst, 1933, **58**, 331) suggests the use of diphenyl carbazide as an absorption indicator, the end point being marked by a colour change from pink to violet. Sulphides interfere with the test, but they are easily removed by shaking the solution with a little lead carbonate and filtration. The usual strength of silver nitrate solution is *N*/10, of which 1 ml. is equivalent to 0·0098 g. $NaCN$. For very dilute cyanide solutions, *N*/100 silver nitrate may be used.

Sulphide is generally estimated by Ewan's method (J.S.C.I. 1909, **28**, 10; *see also* Rossiter, J.S.C.I. 1911, **30**, 583). 10 g. of the finely powdered sample are dissolved in 15 ml. of ordinary water and a lead nitrate solution containing 2·4 g. per litre is run in gradually. The mixture is stirred to coagulate the colloidal lead sulphide into brown flocks, and the addition of lead nitrate continued until a drop of the liquid placed on a filter paper produces no dark coloration with a drop of lead nitrate solution. The results obtained are low, but for small sulphide contents are made sufficiently accurate by taking 1 mol. of the standard lead nitrate solution as equivalent to 0·0007 g. Na_2S (*i.e.* by multiplying the theoretical result by 1·25). The alternative method of sulphide estimation is by precipitating PbS by means of lead carbonate and oxidising the precipitate with boiling nitric acid to $PbSO_4$, which is washed and weighed.

Water is estimated by weighing out about 1 g. of the coarsely powdered sample into a small distilling flask (10–20 ml.), which is then evacuated by a good water pump or by a mercury pump. The flask is then gently warmed, finally to 200–300°C., when the whole of the moisture is expelled in a few minutes without appreciable decomposition of the cyanide.

Carbonate is conveniently estimated by precipitating a suitable portion of the solution with barium chloride in the cold (to avoid decomposition of any cyanate which may be present). The precipitate is washed and titrated, together with the paper, with hydrochloric acid and methyl orange.

Hydroxide may be estimated by a modification of Clennell's method (Chem. News, 1895, **71**, 93). To 100 ml. of the solution, standard $AgNO_3$ solution is added to give a permanent turbidity, excess of $Ba(NO_3)_2$ is then added to precipitate the carbonate, which is filtered off and washed with CO_2-free distilled water, the washings being added to the filtrate. The filtrate is then titrated with standard acid and phenolphthalein.

The Estimation of Chloride is carried out after removing cyanide from the solution by neutralising it with dilute nitric acid, using methyl orange, and boiling for about 1 hour in a draught cupboard. This treatment also decomposes any cyanate present. The chloride remaining is then precipitated by a known excess of standard $AgNO_3$ solution, the $AgCl$ filtered off and the excess of silver back-titrated with ammonium thiocyanate and iron alum in the usual way. If ferrocyanide is present, it may be precipitated with excess of $AgNO_3$ in ammoniacal solution; on acidifying the filtrate with nitric acid, $AgCl$ is precipitated and may be weighed.

Cyanamide in the presence of alkali cyanides is readily estimated by exactly neutralising the solution of 1 g. of the substance in 100–150 ml. of water with nitric acid, and boiling for 20 minutes to expel HCN. After cooling, a few drops of ammonia and then an excess of $AgNO_3$ are added. The canary-yellow precipitate of silver cyanamide is filtered off and dissolved in cold dilute nitric acid, when a small residue of undissolved $AgCN$ is usually left. The silver in the solution is then titrated against ammonium thiocyanate with ferric alum indicator.

This method may be used for cyanamide in the absence of cyanide, when the expulsion of HCN by means of nitric acid may be omitted. For substances rich in cyanamide, it is better to estimate the nitrogen content of the silver cyanamide precipitate by Kjeldahl's method, for although it contains all the cyanamide nitrogen, the precipitate in this case is not pure Ag_2CN_2 (Caro, Z. angew. Chem. 1910, **23**, 2405).

Cyanate is estimated by acidifying the solution with nitric acid and boiling for at least 20 minutes in a draught cupboard. The cyanide is thereby expelled as HCN, and the cyanate is converted into ammonium nitrate and carbon dioxide:

$$HCNO + HNO_3 + H_2O = NH_4NO_3 + CO_2$$

After cooling, the solution is boiled with excess of caustic soda and the ammonia evolved is absorbed in a known excess of standard acid and estimated in the usual way. If cyanamide is present, some ammonia originates from it during the boiling with caustic soda, and in this case Ewan (J.S.C.I. 1904, **23**, 244) suggests that the CO_2 evolved when the sample is boiled with acid should be collected and measured in order to estimate the cyanate.

Analysis of Ferrocyanides.—The most convenient method of ferrocyanide estimation is by titration with a standard zinc sulphate solution. A precipitate containing zinc ferrocyanide is obtained, and the titration is continued until a drop of the solution no longer gives a blue colour with a drop of ferric solution. The procedure is as follows: a solution containing 10·2 g. of $ZnSO_4{\cdot}7H_2O$ and 10 ml. of concentrated sulphuric acid per litre is standardised against a solution of pure potassium ferrocyanide (10 g. $K_4Fe(CN)_6{\cdot}3H_2O$ per litre), 25 ml. of which is mixed with 25 ml. of a saturated solution of K_2SO_4, 25 ml. of water and 10 ml. of 10% sulphuric acid. Equal volumes of the standard zinc and ferrocyanide solutions are required, and the precipitate has the composition $Zn_3K_2[Fe(CN)_6]_2$ (Meurice, Ann. Chim. Analyt. 1913, **18**, 342). Subsequent titrations should be made as nearly as possible under the same conditions. The addition of an excess of potassium sulphate is made with the object of eliminating variations in the composition of the precipitate and thus in the quantity of zinc solution required, depending on the nature of the metal in the ferrocyanide used (Colman, Analyst, 1908, **33**, 261; J.S.C.I. 1908, **27**, 806; *see also* Treadwell and Chervet, Helv. Chim. Acta, 1923, **6**, 559).

Feld's mercuric cyanide method (J. für Gasbeleuchtung, 1903, **46**, 565; J.S.C.I. 1903, **22**, 1068) is more accurate. Ferrocyanide equivalent to 0·3–0·5 g. of yellow prussiate is boiled with 10 ml. of N-$NaOH$ and 15 ml. of $3M$-$MgCl_2$ solution (285 g. $MgCl_2$ per litre). The boiling is continued for 10 minutes to expel any cyanide completely as HCN, after which 100 ml. of boiling $N/10$-$HgCl_2$ solution are run in, and the boiling continued for 10 minutes to convert the ferrocyanide into mercuric cyanide. The mixture is then distilled for 30 minutes with 30 ml. of $3N$-H_2SO_4, the HCN evolved being absorbed in caustic soda and the cyanide in the resulting solution titrated with $AgNO_3$, using KI as indicator. Williams (J.S.C.I. 1912, **31**, 468) avoids the conversion of ferrocyanide into mercuric cyanide by making use of the catalytic action of cuprous chloride, 0·05–0·10 g. of the pure compound dissolved in HCl being added to the ferrocyanide solution after expelling HCN by boiling with $MgCl_2$ (as above) or with $Pb(NO_3)_2$, which also removes sulphide. On boiling the mixture for 30 minutes, the CN of the ferrocyanide is quantitatively removed as HCN.

Analysis of Thiocyanates.—Volhard's method, namely, the precipitation of insoluble silver thiocyanate by the addition of $AgNO_3$ to a thiocyanate solution which is neutral or acid with nitric acid, is used. The end point is determined by adding a small amount of a ferric salt to the solution before titrating, the disappearance of the red colour due to ferric thiocyanate indicating that the precipitation of the thiocyanate as silver salt is complete. A quantity of the solution containing about 0·25 g. of thiocyanate is diluted to 100–150 ml. with distilled water, acidified with 10 ml. of dilute HNO_3, and 5 ml. of a 10% $Fe(NO_3)_3$ solution are added. The mixture is titrated with $N/10$-$AgNO_3$ solution. In analysing a gas works product for thiocyanate, ferrocyanide is first removed by slightly acidifying the solution and adding ferric alum. The filtrate is treated with acid sodium sulphite in excess, then with copper sulphate, and is boiled for a few minutes. The precipitate of cuprous thiocyanate, which may be mixed with copper sulphide, is filtered off, washed with boiling water, and digested with excess of caustic soda. Cuprous hydroxide and sodium thiocyanate solution are formed, the latter being separated by filtration and titrated by Volhard's method above.

Analysis of Gas Works Products.—Cyanide and ferrocyanide in gas purification masses are determined by triturating 30–40 g. of the material in a mortar with excess of cold caustic soda solution for several hours. A little $FeSO_4$ may be added to convert cyanide into ferrocyanide. The filtrate is treated with 4–5 times its volume of methylated spirit, which precipitates all the sodium ferrocyanide present but retains carbonyl ferrocyanide (*see* p. 477), thiocyanate, sulphide, and excess of caustic soda in solution. The precipitate is then treated as described above (Colman, Analyst, 1908, **33**, 261; J.S.C.I. 1908, **27**, 806; Skirrow, J.S.C.I. 1910, **29**, 319).

The small quantities of cyanogen compounds in concentrated ammonia liquor may be estimated by converting them into ferric thiocyanate and measuring the depth of colour by means of a tintometer (Spielmann and H. Wood, J.S.C.I. 1919, **38**, 43T, 369T). Thiocyanate initially present is first estimated by acidifying the diluted sample with H_2SO_4 in the cold, and removing ferrocyanide by means of a small excess of iron alum; a large excess of iron alum is then added to the filtrate, which is examined in the tintometer. Cyanide is next converted into thiocyanate by digestion at 30–35°C. with ammonium polysulphide solution, and a second estimation of the depth of colour is made. Thiocarbonate is converted into thiocyanate by digestion at 70–75°C. for 45 minutes with NH_3, cyanide and ferrocyanide being unaffected.

The HCN content of coal gas is generally determined by treating the gas with ammonium polysulphide solution, when thiocyanic acid, $HCNS$, is formed and can be estimated as thiocyanate (*see* Voituret, Brennstoff-Chem. 1932, **13**, 264; Pieters and Penners, Het Gas, 1932, **52**, 382). Alternatively the gas may be washed with a mixture of caustic soda, ferrous sulphate, and water (as in a cyanide washer) to obtain the HCN in the form of ferrocyanide, which can be estimated by the mercuric cyanide method already described. An account of different methods for the determination of HCN in coal gas is given by Brender à Brandis and Bohlken, Het Gas, 1933, **53**, 194.

G. E. W.

CYANIDIN is the most common and widely distributed of the anthocyan pigments of plants, and occurs naturally in the form of various glycosides.

It was first isolated by Willstätter and Everest (Annalen, 1913, **401**, 189) from the blue cornflower pigment *cyanin*, and may be obtained by hydrolysis of this or any other of its naturally occurring glycosides, or from its methyl ether, peonidin, by demethylation. Glucoside-pigments derived from cyanidin have been isolated from, or detected in, the flowers of blue and deep purple cornflowers, *Rosa gallica*, peony, chrysanthemum, dahlia (deep red), aster, poppy, *Zinnia elegans*, gladiolas (hybrid), *Gaillardia bicolor*, *Helenium autumnale*, *Tulipa Gesneriana*, *Tropæolum maius*, and in the fruits, or berries, of the sweet cherry, sloe, cranberry, red currant, raspberry and mountain ash. In some cases they are accompanied by derivatives of other anthocyanidins (*see* various papers by Willstätter and his collaborators).

Apart from the qualitative identification of cyanadin glycosides in nearly two hundred different flowers and fruit by G. and R. Robinson (Biochem. J. 1931, **25**, 1687; 1932, **26**, 1647; 1934, **28**, 1712), more recent isolation and analysis of cyanidin pigments includes that from the crimson antirrhinum by Scott-Moncrieff (Biochem. J. 1930, **24**, 753), elderberry skins and flowering currant by Nolan and Casey (Proc. Roy. Irish Acad. 1931, **40B**, 56; 1936, **43B**, 1), American cranberries by Grove and Robinson (Biochem. J. 1931, **25**, 1706), blackberries by Karrer and Pieper (Helv. Chim. Acta, 1930, **13**, 1067), violet-coloured radishes by Schudel (Dissertation, Zürich, 1918), shiso leaves by Chika Kuroda and Mizu Wada (Proc. Imp. Acad. Tokyo, 1935, **11**, 28), maize by Sando, Milner, and Sherman (J. Biol. Chem. 1935, **109**, 203), and hibiscus by Yamamoto and Oshima (Sci. Papers Inst. Phys. Chem. Research, Tokyo, 1932, **19**, 134).

The natural glycosides of cyanidin already known are the 3-glucosides *chrysanthemin*, etc., the 3-galactoside *idaein* the 3-diglucoside *mekocyanin*, the 3-rhamnoglucosides *keracyanin*, *antirrhinin*, etc., the 3:5-diglucoside *cyanin*, the 3-pentoside *hibiscin*, and the bimolecular glucoside and pentoside *sambucicyanin*. Acylated glycosides also occur.

Cyanidin chloride, $C_{15}H_{11}O_6Cl$, 3:5:7-trihydroxy-2-*m*:*p*-dihydroxyphenyl-1:4-benzopyranol-anhydrochloride crystallises readily from 20% HCl when its pure glucosides are hydrolysed by boiling with this reagent for 3 minutes; the crystals, long red-brown needles with metallic lustre, contain $1H_2O$, which is very difficult to remove, complete drying being only obtained at 105°C. in high vacuum. The anhydrous salt does not melt below 300°C.; if dried at 50°C. it melts at once if dipped into a bath at 220°C., but does not melt if put in at 200°C. and the temperature then gradually raised. It is very soluble in methyl or ethyl alcohol; fairly soluble in dilute sulphuric acid; difficultly soluble in HCl. Neutral alcoholic or aqueous solutions lose their colour on standing owing to *pseudo*-base formation, acids reproduce colour, slowly if cold, rapidly if warm. The absorption spectrum shows one broad band with ill-defined edges.

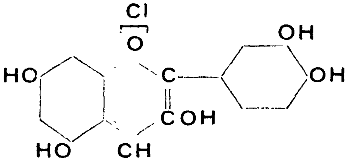
Cyanidin colour base separates in crystalline condition when a hot concentrated solution of the chloride in alcohol is mixed with twice its volume of water (*cf.* Willstätter and Nolan, Annalen, 1915, **408**, 13). It is fairly soluble in alcohol or pyridine.

Cyanidin pseudo base, $C_{15}H_{12}O_7$, crystallises with $1H_2O$ when a dilute solution of the chloride in alcohol is mixed with twice its volume of water, warmed gently, then, after it has become colourless, evaporated *in vacuo*, extracted with ether, and the product crystallised from water. Readily soluble in water, alcohol, acetone or glacial acetic acid, it is insoluble in benzene; with soda it gives a yellow coloration, with HCl cyanidin chloride is formed and crystallises out. When decomposed by means of fused alkali, protocatechuic acid and phloroglucinol are produced.

Cyanidin chloride dyes wool (tin mordant) blue-violet, cotton (tannined) violet, and unmordanted wool fine rose (Willstätter and Mallison).

Qualitative analytical tests for cyanidin include the reddish-violet colour of its amyl alcohol solutions on shaking with sodium acetate, turning to a pure blue with a drop of ferric chloride, the incomplete extraction by the "cyanidin reagent" and "delphinidin reagent," the moderate resistance to oxidation in alkaline solution, and the complete precipitation from amyl alcohol by 5–6 volumes of benzene. Cyanidin can also be identified by the specific colour reactions of its various glycosides (G. Robinson and R. Robinson, *ibid.*).

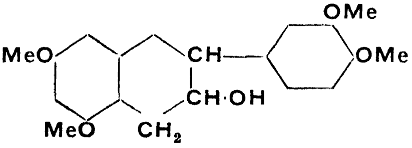
Many different syntheses of cyanidin have now been carried out, and these confirm the structure of the chloride which was first put forward by Willstätter and Everest. The claims of Nierenstein and Malkin (Ber. 1928, **61**, B, 791; J. Amer. Chem. Soc. 1930, **52**, 2864) that natural cyanidin chloride is not correctly represented by this accepted formula, have been dealt with by Robinson and Robertson (J.C.S. 1928, 1503), Robinson (Chem. Age, 1928, **19**, 337), Willstätter and Robinson (Ber. 1928, **61**, [B], 2504), Kuhn-Jauregg (*ibid.* 2506).



The first synthesis was carried out by reduction of the related flavonol quercetin by Everest (Proc. Roy. Soc. 1914, **87**, B, 444; 1914, **88**, B, 326) and by Willstätter and Mallison (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1914, 769). More recently Asahina and Inubuse, using sodium amalgam in alkaline solution, have obtained cyanidin by the reduction of rutin (3-rhamnoglucoside of quercetin) and also, with more difficulty, of quercetin itself (Ber. 1931, **64**, B, 1256). Karrer, Yeu, and Reichstein (Helv. Chim. Acta, 1930, **13**, 1308) have obtained small yields, using titanium trichloride as a reducing agent. Anthocyanidins have also been obtained from flavones by Kaoru Kondo and Hisao Segawa (J. Pharm. Soc. Japan, 1932, **52**, 353, 358).

Willstätter, Zechmeister and Kindler (Ber. 1924, **57**, [B], 1938) synthesised cyanidin chloride using trimethoxycoumarin, and magnesium 3:4-dimethoxyphenyl iodide, and Robinson and his collaborators have also synthesised it by various methods, the most satisfactory (J.C.S. 1928, 1526) involving the use of O-benzoylphloroglucinaldehyde.

Appel and Robinson (J.C.S. 1935, 426) have obtained pure cyanidin chloride by oxidation of tetramethyl-*d*-catechin by treatment with bromine followed by demethylation with hydriodic acid and phenol. Freudenberg, Fikentscher, Harder, and Schmidt (Annalen, 1925, **444**, 135), on the other hand, have obtained small yields of *dl-epi*catechin from cyanidin.



The investigations by G. and R. Robinson (Biochem. J. 1933, **27**, 206; 1934, **28**, 1712) on the existence and occurrence of leuco-anthocyanins show that the greater proportion give cyanidin chloride on treatment with hot hydrochloric acid.

In the case of such natural substances as the anthoxanthins (flavones and flavonols), tannins, catechins, and leuco-anthocyanins, as well as the anthocyanins, the 3′:4′-dihydroxy grouping is by far the most common, a fact which affords a more reasonable explanation for the co-production of glycosides of cyanidin and the related flavonol quercetin in rose, wallflower and maize than the suggestion of Everest (Proc. Roy. Soc. B, 1918, **90**, 251) and Sando (*l.c.*) that the cyanidin in these plants is derived directly from quercetin. The inverse correlation in the production of cyanidin and the unrelated flavone apigenin in *Antirrhinum* (Scott-Moncrieff, *l.c.*) and *Dahlia* (Lawrence and Scott-Moncrieff, J. Genetics, 1935, **30**, 155) points rather to the metabolism of anthocyanins and anthoxanthins by parallel syntheses, each pigment being partially derived from a common component whose availability is strictly limited (Scott-Moncrieff, *ibid.* 1936, **32**, 117).

The genetical relationship between cyanidin pigmentations and those by the more oxidised delphinidin and the less oxidised pelargonidin is such that, when general anthocyanin production occurs, the more oxidised type is dominant to the less oxidised, and is also deeper and more blue-toned, *e.g.* in sweet pea the purple flower contains the delphinidin, the paler red the cyanidin, and the even paler salmon the pelargonidin type of anthocyanin (Scott-Moncrieff, *ibid.* 1936, 32, 117).

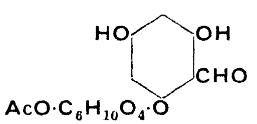
R. S.-M.

CYANIN, the anthocyan pigment of blue or purple cornflowers, also occurs in *Rosa gallica*, deep red dahlias, brown wallflowers, etc. It is a diglucoside of cyanidin yielding cyanidin (1 mol.) and glucose (2 mols.) on hydrolysis. Willstätter and Everest (Annalen, 1913, **401**, 189) first obtained it in a pure condition, as the crystalline chloride, from the blue cornflower; it is, however, more readily prepared from *Rosa gallica* (Willstätter and Nolan, Annalen, 1915, **408**, 1), or the deep red dahlia (Willstätter and Mallison, Annalen, 1915, **408**, 147). The *chloride*, $C_{27}H_{31}O_{16}Cl$, red-brown rhombic leaflets containing 2½ mols. of water, can only be completely dried at 105°C. in high vacuum. Air-dried it is very difficultly soluble in water, acetone or chloroform, difficultly soluble in cold alcohol or dilute HCl, insoluble in benzene. In 7% sulphuric acid it is fairly soluble, but the sulphate separates out from the solution. Soda added to an acid solution gives a pure blue and sodium acetate a violet colour; ferric chloride gives a fine blue in alcohol, violet in water. It shows a single absorption band covering the green and blue; it is optically active. Willstätter and

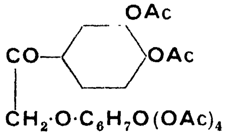
Nolan give, for white light, $[a] = -258°$ ($\pm 10°$). The low "distribution number" (partition value between amyl alcohol and aqueous HCl) is normal for a diglycoside. *Picrate*, red needles, very soluble in water. *Cyanin potassium salt*, the blue pigment of the cornflower, was obtained crystalline, but not free from $NaCl$, by Willstätter and Everest, after purification by dialysis. It is very soluble in water, insoluble in alcohol; its blue aqueous solutions become colourless on standing owing to formation of a *pseudo-* base, whereas in 20% $NaCl$ solution the colour is stable for months.

Cyanin was the first anthocyan to be isolated and successfully analysed. It is very widely distributed. G. and R. Robinson (Biochem. J. 1931, **25**, 1687; 1932, **26**, 1647; 1934, **28**, 1712) have shown by their qualitative tests on hundreds of flowers and fruits that cyanin with its dihydroxy grouping is by far the most common type, as is also the case with other flavan substances. Cyanin has also been isolated from brown wallflowers by Scott-Moncrieff (Chem. Ind. Rev. 1929, **7**, 630) and from shiso leaves by Chika Kuroda and Mizu Wada (Proc. Imp. Acad. Tokyo, 1935, **11**, 28), who found that here it was sometimes combined with *p*-coumaric acid.

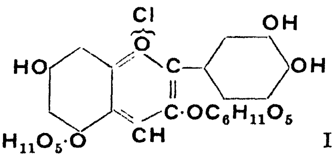
The position of the glucose molecules was uncertain for some time, Robinson favouring the 5-position and Karrer the 3. These apparently opposing views have been united by Robinson's recognition that cyanin, pelargonin, peonin, malvin, petunin and delphin are all 3:5-dimonosides (J.C.S. 1931, 2665). This was confirmed by the synthesis of 3:5-β-diglucosidyl cyanidin chloride (III) by Todd and Robinson (J.C.S. 1932, 2293) by condensation of 2-O-monoacetylglucosidylphloroglucinaldehyde (I) and ω-O-tetra-acetyl-β-glucosidoxy-3:4-diacetoxy-acetophenone (II), and subsequent deacetylation with KOH.



I.

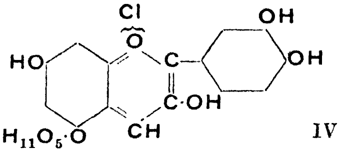


II.



III.

The 5-monoglucoside, *cyanenin* (IV), which is not known to occur naturally, can be obtained from cyanin by partial hydrolysis and has also been synthesised by Léon and Robinson (J.C.S. 1932, 2221).



IV.

Since the p_H of the cell sap of blue cornflowers is slightly more acid than that of the red *Rosa Gallica*, the blueness of the former may be dependent upon a colloidal phenomenon (G. and R. Robinson, Nature, 1933, **132**, 626).

R. S.-M.

CYANINE BLUE, *Leitch's blue*. A "mixed" pigment of cobalt blue and Prussian blue.

CYANINE DYES. The first cyanine dye, prepared in 1856, appeared at the time to be valueless owing to its instability to light. In 1873 Vogel discovered that various dyes, amongst them cyanine, possess the power of rendering photographic plates, which normally are sensitive only to light of short wave-length, sensitive also to other wave-lengths, the sensitising maximum approximating to the absorption maximum of the dye (Ber. 1875, **8**, 1635). Whilst very interesting scientifically, even this action of cyanine seemed at the time to have little practical value, since it was accompanied by veiling and staining of the plate. In 1903, however, it was found that the related *iso*cyanines sensitise, without accompanying defects, and a flood of German patents was the result, whilst the German chemists arrived at the chemical structures of cyanine and *iso*cyanine. At the time of the Great War, it was necessary that the Allied Armies should have photographic sensitisers, because they are essential for aeroplane photography. This led Mills to his study of the cyanines, and he and his pupils established the structure of the whole group; thus *Pinacyanol*, then the best sensitiser for red light, had been discovered in 1905, but its constitution was not elucidated until 1920, and *Thiazole Purple*, discovered in 1887, was of unknown structure until Mills's publication in 1922. The preparation of cyanines containing nuclei other than the original one, quinoline, greatly enlarged the field, as did observations that the new types of cyanines also had valuable photographic properties; some of them are greatly superior to the older types.

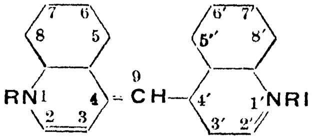
At present certain cyanines, absorbing light of comparatively short wave-length, are used for conferring extra-sensitivity upon gelatino-chloride photographic emulsions, such as are used for coating gaslight printing papers; others, absorbing longer wave-lengths, are used to sensitise gelatino-bromide photographic emulsions, such as are used for plates and films, to any desired part, or to the whole, of the visible spectrum; lengthening the chain which joins the nuclei in the cyanine molecule has made feasible the preparation of infra-red sensitive photographic material, which is useful for distance photography and for certain kinds of scientific work. The cyanine dyes have not only proved valuable to astronomers and other scientists, but also to the world at large, for their power of conferring sensitivity to light of various colours has made possible a true rendering of colour in monochrome and led to a great increase of speed, especially to artificial light. The high achievements of modern photography are in fact largely due to photographic sensitisers, of which the cyanines are amongst the most important. Sensitisers have also made possible photography in colour.

Cyanines (*4:4′-Cyanines*), iso*Cyanines* (*2:4′-Cyanines*), and *ψ-Cyanines* (*2:2′-Cyanines*).—The blue dye, *cyanine* (*Quinoline Blue*), was prepared by Greville Williams by the action of caustic alkali on the alkiodide of impure quinoline (Trans. Roy. Soc. Edin. 1856, **21**, 377; Chem. News, 1859, **1**, 15; 1860, **2**, 219). Hofmann recognised that this quinoline contained lepidine (Proc. Roy. Soc. 1863, **12**, 410), and Hoogewerff and van Dorp showed that the ethiodides of the two bases condense, under the influence of potassium hydroxide in aqueous solution, to form the cyanine molecule according to the equation

$$C_9H_7N{\cdot}C_2H_5I + C_{10}H_9N{\cdot}C_2H_5I = C_{23}H_{23}N_2I + H_2 + HI$$

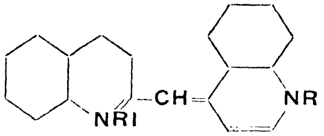
(Rec. trav. chim. 1883, **2**, 28, 41, 317; 1884, **3**, 337). They found that a purple dye, iso*cyanine*, is produced by the action of alkali on the alkiodides of quinoline and quinaldine, and they represented its formation similarly (*ibid.* 1883, **2**, 317; 1884, **3**, 337). Spalteholz independently discovered the *iso*cyanines, but regarded them as containing two extra hydrogen atoms (Ber. 1883, **16**, 1847). He, and also Hoogewerff and van Dorp, pointed out that, in preparing cyanines and *iso*cyanines, it is advantageous to use twice the calculated amount of quinoline alkiodide. Miethe and Traube's discovery of the value of the *iso*cyanines as photographic sensitisers (G.P. 142926, 1902) led to patents by various German firms, in which substituents were introduced to improve the sensitising action, and the acid radical was altered so as to increase the solubility (G.P. 158078, 167159, 167770, 170048, 170049, 1903). This was largely the work of E. König. *iso*Cyanines have appeared upon the market under the names *Ethyl Red*, *Homocol*, *Isocol*, *Orthochrome T*, *Pericol*, *Pinachrome*, *Pinachrome Violet*, *Pinaverdol* and *Sensitol Green*, whilst cyanines were marketed under the names *Ethyl Cyanine T* and *Quinoline Blue*.

The first suggestion as to the constitution of cyanines and *iso*cyanines was made by Decker, who had discovered the alkylquinolinium pseudobases and regarded these as intermediates (Ber. 1891, **24**, 690). Miethe and Book formulated the *iso*cyanine molecule as having two quinoline nuclei linked in the 2:4′-positions to a :CH group (Ber. 1904, **37**, 2008), but with two extra hydrogen atoms as suggested by Spalteholz. It was W. König who pointed out how unlikely is their presence and he gave formulæ for cyanine (I) and *iso*cyanine (II) which are accepted to-day, the former with a 4:4′-linking, the latter with a 2:4′-linking (J. pr. Chem. 1906, [ii], **73**, 100). König made the alternative suggestion that in cyanine and *iso*cyanine one quinoline ring may have undergone fission to an open chain (*ibid.* 1912, [ii], **86**, 166), but this was disproved by Mills and Evans's synthesis of *o*-aminocinnamylidenequinaldine methiodide, in structure very close to the open-chain formula for *iso*cyanine, but differing in properties (J.C.S. 1920, **117**, 1035), and further evidence against it was advanced by König and Treichel (J. pr. Chem. 1921, [ii], **102**, 63). Vongerichten and Höfchen produced evidence that the 2-methyl group of quinaldine is concerned in *iso*cyanine formation (Ber. 1908, **41**, 3054), whilst Kaufmann and Vonderwahl proved that the 4-position of the quinoline nucleus is involved (Ber. 1912, **45**, 1404). The constitution of *iso*cyanine (III) was definitely established by Mills and Wishart, by its oxidation to 1-alkyl-2-quinolone and cinchonic acid alkochloride (J.C.S. 1920, **117**, 579), whence that of cyanine follows. The formula of *iso*cyanine is confirmed by Adams and Haller's preparation of various *iso*cyanines by the action of alkali on various lepidine alkiodides (J. Amer. Chem. Soc. 1920, **42**, 2389), and by Hamer's synthesis from lepidine ethiodide and 2-iodoquinoline ethiodide (J.C.S. 1928, 206). She subsequently prepared complex *iso*cyanines from 5-methylacridine methiodide and 2-iodo-



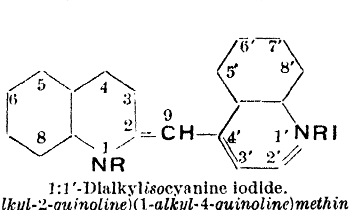
1:1′-Dialkylcyanine iodide.
Bis-(1-alkyl-4-quinoline)methincyanine iodide.[1]

I.



1:1′-Dialkyl*iso*cyanine iodide.
(1-Alkyl-2-quinoline)(1-alkyl-4-quinoline)methincyanine iodide.

II.



1:1′-Dialkyl*iso*cyanine iodide.
(1-Alkyl-2-quinoline)(1-alkyl-4-quinoline)methincyanine iodide.

III.

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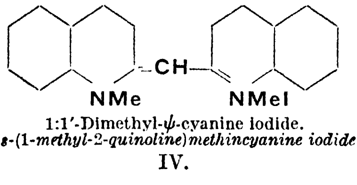
[1] See p. 530 for explanation of alternative nomenclature for this and subsequent compounds.

quinoline alkiodide, but these were not sensitisers (J.C.S. 1930, 995). For accounts of the preparation of *iso*cyanines, by the action of caustic alkali on alcoholic solutions of quaternary salts of substituted quinolines and quinaldines, and of their properties, including optical and photographic properties, *see* Sheppard (J.C.S. 1909, **95**, 15), Wise, Adams, Stewart and Lund (Ind. Eng. Chem. 1919, **11**, 460), Mills and Pope (Phot. J. 1920, **60**, 183), Barbier (Bull. Soc. chim. 1920, [iv], **27**, 427), Hamer (J.C.S. 1921, **119**, 1432; Phot. J. 1922, **62**, 8), and Sakurai (Bull. Inst. Phys. Chem. Res. Japan, 1932, **11**, 681, 1044); Hamer prepared complex *iso*cyanines from quinoline alkiodide and 2-methylacenaphthpyridine methiodide (J.C.S. 1930, 995).

In naming *iso*cyanines, plain numerals refer to the quinaldine nucleus, whilst those of the quinoline nucleus are followed by a dash (Mills and Pope, Phot. J. 1920, **60**, 183). Mills and Wishart's formula for *iso*cyanine (III) differs from König's (II) in that the acid radical is attached to the alternative nitrogen atom, with a corresponding difference in the conjugated chain uniting the nitrogen atoms. Mills and Wishart suggested that the two formulæ represent virtually tautomeric compounds (J.C.S. 1920, **117**, 579), and *virtual tautomerism* has since been shown to be a characteristic of cyanines of various types (Mills and Braunholtz, *ibid.* 1922, **121**, 1489; Hamer, *ibid.* 1928, 206; Kuhn, Winterstein and Balser, Ber. 1930, **63**, [B], 3176; Ogata, Proc. Imp. Acad. Tokyo, 1932, **8**, 119; Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 549; Brooker and Keyes, J. Amer. Chem. Soc. 1935, **57**, 2488). Although the acid radical in cyanines is not now regarded as attached to one nitrogen atom, to the exclusion of the other, static formulæ are given throughout this article, for the sake of clearness. For the convenience of naming definite examples, the anion in the formulæ is usually represented as iodide, although other anions are equally applicable.

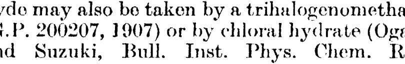
The cyanines, to use the term in its general sense, are monacid salts which can conveniently be crystallised from methyl or ethyl alcohol, but are only slightly soluble in hot water. The crystals usually contain solvent of crystallisation; they have a metallic lustre and are often pleochroic. Although the solutions are decolorised by excess of acid, the colourless diacid salts are unstable.

Although the 4:4′- and 2:4′-cyanines have been known from such an early date, the preparation of 2:2′-cyanine (IV) by Fischer and Scheibe, by condensing 2-iodoquinoline methiodide with quinaldine methiodide (J. pr. Chem. 1920, [ii], **100**, 86) is much more recent. Instead of their term "*ψ-isocyanine*," Mills and Odams proposed the name *ψ-cyanine* (J.C.S. 1924, **125**, 1913). By effecting the condensation under modified conditions, Hamer prepared a number of 2:2′-cyanines and noted that these also are photographic sensitisers (J.C.S. 1928, 206). For the preparation of more complex *ψ*-cyanines, 2-iodo-*β*-naphthaquinoline alkiodide was condensed with an alkiodide of quinaldine or *β*-naphthaquinaldine (Hamer and Kelly, *ibid.* 1931, 777), and 2-iodoquinoline alkiodide was condensed with 2-methylacenaphthpyridine methiodide (Hamer, *ibid.* 1930, 995). The I.G. Farbenind. A.-G. prepared the diethyl analogue of IV from 1-ethyl-2-thioquinolone ethiodide and quinaldine ethiodide in pyridine (B.P. 423792, 1932), whilst Kendall prepared IV from 2-methylthiolquinoline, methyl *p*-toluenesulphonate, and malonic acid in pyridine, followed by potassium iodide (B.P. 431141, 1933).



1:1′-Dimethyl-*ψ*-cyanine iodide.
Bis-(1-methyl-2-quinoline)methincyanine iodide.
IV.

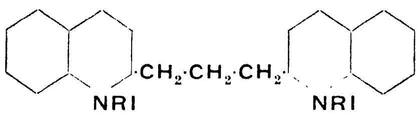
2:2′-, 2:4′-, and 4:4′-*Carbocyanines.*—The most valuable sensitiser of its day, conferring photographic sensitivity even to red light, was the blue dye *Pinacyanol*, which was discovered by Homolka and patented by the Farbwerke vorm. Meister, Lucius and Brüning (G.P. 172118, 1905) (later known also as *Quinaldine Blue* and *Sensitol Red*; *Naphthacyanole*, *Pinachrome Blue* and *Sensitol Violet* belong to the same class). It was prepared by the action of caustic alkali on an alcoholic solution of quaternary salts of quinoline and quinaldine, in the presence of formaldehyde. The part played by formaldehyde may also be taken by a trihalogenomethane (G.P. 200207, 1907) or by chloral hydrate (Ogata and Suzuki, Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 488). The preparation of pinacyanol and its homologues ("*ψ-dicyanines*"), by the formaldehyde method, is described by O. Fischer (J. pr. Chem. 1918, [ii], **98**, 204), Wise, Adams, Stewart and Lund (Ind. Eng. Chem. 1919, **11**, 460), Mills and Pope (Phot. J. 1920, **60**, 253), Braunholtz (J.C.S. 1922, **121**, 169), Moudgill (*ibid.* 1922, **121**, 1509), Mees and Gutekunst (Ind. Eng. Chem. 1922, **14**, 1060), and Hamer (J.C.S. 1923, **123**, 2333). Fischer observed that the quinoline salt takes no direct part in the condensation (*l.c.*); although it has always been accredited with increasing the yield, a recent publication denies this (Lauer and Horio, J. pr. Chem. 1935, [ii], **143**, 305). The formula (V) for pinacyanol was suggested by Mills and Pope (*l.c.*) and established by Mills and Hamer, who concluded from analysis that the compound is formed according to the equation



1:1′-Diethyl-2:2′-carbocyanine iodide.
Bis-(1-ethyl-2-quinoline)trimethincyanine iodide.
V.

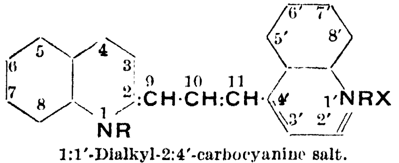
$$2C_{10}H_9N\cdot C_2H_5X + CH_2O = C_{25}H_{25}N_2X + H_2O + HX + 2H,$$

and who found that on oxidation it gives quinaldinic acid and 1-ethyl-2-quinolone (J.C.S. 1920, **117**, 1550). Their formula was confirmed by König's preparation from quinaldine ethiodide and ethyl orthoformate in the presence of acetic anhydride (Ber. 1922, **55**, [B], 3293); Hamer, by using pyridine instead of acetic anhydride, obtained 70–79% yields by this method (J.C.S. 1927, 2796), and further confirmed formula V by converting methylenediquinaldine dialkiodide (VI) into (V), by the action of alkali in the presence of a quinolinium salt (J.C.S. 1923, **123**, 246), and by reducing (V) to (VI) (J.C.S. 1925, **127**, 211); a process for converting (VI) into (V) by treatment with an oxidising agent in a non-alkaline medium was subsequently patented (Soc. Chem. Ind. in Basle, B.P. 321155, 1928). Rosenhauer with Hoffmann and Unger (Ber. 1926, **59**, [B], 946) obtained the methylene bases from quinaldinium salts in the solid state. By condensing such a base with iodoform, the 2:2′-carbocyanine (V) was synthesised by Fischer and Rosenhauer (Z. angew. Chem. 1923, **36**, 330) and by Rosenhauer, Schmidt and Unger (Ber. 1926, **59**, [B], 2356). Kuhn and Winterstein prepared 2:2′-carbocyanines, otherwise difficult to obtain, by the action of acetic anhydride and sodium formate on the appropriate methylene base, or on its salt with an organic acid (B.P. 328357, 1929). Sakurai has described the sensitising action of certain 2:2′- (and 2:4′-) carbocyanines (Bull. Inst. Phys. Chem. Res. Japan, 1932, **11**, 1044), and Kendall the preparation of a 2:2′-carbocyanine, from 2-methylthiolquinoline, alkyl *p*-toluenesulphonate, glutaconic acid, and pyridine (B.P. 431141, 1933). Ogata, Kawasaki and Masuda prepared a 2:2′-carbocyanine containing two nuclei isomeric with phenanthroline from a salt of the appropriate base, ethyl orthoformate, and acetic anhydride (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 486); for preparing a simple 2:2′-carbocyanine, Ogata and Suzuki treated quinaldine methiodide with chloral hydrate and alkali (*ibid.* 488).



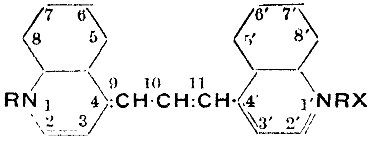
Methylenediquinaldine dialkiodide.

VI.



1:1′-Dialkyl-2:4′-carbocyanine salt.
(1-*Alkyl*-2-*quinoline*)(1-*alkyl*-4-*quinoline*)*trimethincyanine salt.*

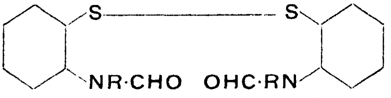
VII.



1:1′-Dialkyl-4:4′-carbocyanine salt.
Bis-(1-*alkyl*-4-*quinoline*)*trimethincyanine salt.*

VIII.

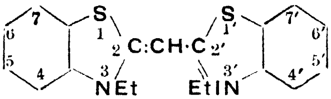
When the constitution of pinacyanol was established as (V), Mills and Hamer predicted that, corresponding with this 2:2′-carbocyanine, there would also be a 2:4′- and a 4:4′-carbocyanine (VII and VIII) (J.C.S. 1920, **117**, 1550) This prediction was soon fulfilled, for Mills and Braunholtz synthesised (VIII) (J.C.S. 1923, **123**, 2804), whilst Mills and Odams synthesised (VII) (*ibid.* 1924, **125**, 1913). Thus Mills and Braunholtz showed that when quinaldine ethonitrate is condensed with di-*o*-formylalkylaminodiphenyl disulphide (IX), in pyridine solution, one product is (V), the disulphide having furnished the central carbon atom of the three-carbon chain; when lepidine ethonitrate is used instead of quinaldine ethonitrate, the corresponding product must be (VIII). They identified this dye with *Kryptocyanine* (also called *Rubrocyanine*), which Adams and Haller had prepared by using a lepidinium instead of a quinaldinium salt in the carbocyanine condensation (J. Amer. Chem. Soc. 1920, **42**, 2661), and which has proved a valuable sensitiser for infra-red light. By interaction of lepidinium salts, pyridine and ethyl orthoformate, Hamer prepared 4:4′-carbocyanines (J.C.S. 1927, 2796), together with *neo*cyanine (*q.v.*). Mills and Odams, by the action of (IX) on a mixture of the ethonitrates of quinaldine and lepidine, synthesised the 2:4′-carbocyanine (VII). From a spectroscopic examination they concluded that the *dicyanine*, which had been prepared from quaternary salts of 2:4-dimethylquinoline and its derivatives (G.P. 155541, 1903; Fischer, J. pr. Chem. 1918, [ii], **98**, 204; Wise and Adams, Ind. Eng. Chem. 1918, **10**, 801; Mikeska, Haller and Adams, J. Amer. Chem. Soc. 1920, **42**, 2392; Palkin, Ind. Eng. Chem. 1923, **15**, 379), is a 2:4′-carbocyanine.



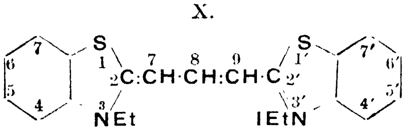
Di-*o*-formylalkylaminodiphenyl disulphide.

IX.

Thiacyanines, *Thiacarbocyanines*, *Thia-2′-cyanines* (*Thia-ψ-cyanines*), and *Thia-4′-cyanines* (*Thia*iso*cyanines*).—Hofmann observed that a purple dye, which he regarded as the cyanine of the benzthiazole series, is formed by heating an aqueous solution of the alkiodides of benzthiazole and 2-methylbenzthiazole with ammonia (Ber. 1887, **20**, 2251). Mills showed that the reaction proceeds more readily in pyridine and isolated a yellow compound in addition to the purple one. Analyses led him to the surprising conclusion that the yellow dye is the cyanine (X), and the purple dye the carbocyanine (XI), of the benzthiazole series, and this was confirmed by synthesising the *thiacyanine* (X). (XI) sensitised a gelatino-bromide and (X) a gelatino-chloride photographic emulsion (J.C.S. 1922, **121**, 455). The name *thia-*



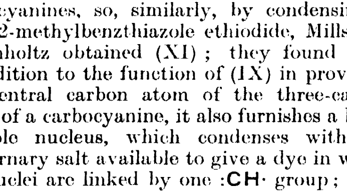
3:3′-Diethylthiacyanine iodide.
Bis-(3-ethyl-2-benzthiazole)methincyanine iodide.
X.



3:3′-Diethylthiacarbocyanine iodide.
Bis-(3-ethyl-2-benzthiazole)trimethincyanine iodide.
XI.

cyanine is in accordance with international nomenclature and therefore preferred to the original term "*thiocyanine.*" Similarly, the original name "*carbothiocyanine*" for (XI) was first replaced by "*thiocarbocyanine*" (Hamer, J.C.S. 1927, 2796), and has now become *thiacarbocyanine.* The thiacyanine (X) corresponds with *ψ*-cyanine, *iso*cyanine, and cyanine, and the thiacarbocyanine (XI) with the 2:2′-, 2:4′-, and 4:4′-carbocyanines. Just as the disulphide (IX) was used to synthesise 2:2′-, 2:4′-, and 4:4′-carbocyanines, so, similarly, by condensing it with 2-methylbenzthiazole ethiodide, Mills and Braunholtz obtained (XI); they found that, in addition to the function of (IX) in providing the central carbon atom of the three-carbon chain of a carbocyanine, it also furnishes a benzthiazole nucleus, which condenses with the quaternary salt available to give a dye in which the nuclei are linked by one :**CH**· group; thus from (IX) and 2-methylbenzthiazole ethiodide, the other product is (X) (*ibid.* 1923, **123**, 2804).

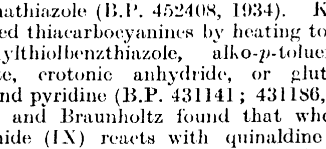
Fisher and Hamer prepared *thiacyanines* from a 2-methylbenzthiazolium or a 1-methyl-*α*-naphthathiazolium chloride, by the action of amyl nitrite in the presence of acetic anhydride, (J.C.S. 1930, 2502). The I.G. Farbenind. A.-G. applied this method to the preparation of thiacyanines with complex nuclei (B.P. 400401, 1931), and also described aminothiacyanines (B.P. 400951, 1931). König, Kleist and Götze prepared thiacyanines, including one (XII) of considerable complexity, by treatment of 3-methylbenzthiazolone, or its derivatives, with magnesium methyl iodide (Ber. 1931, **64**, [B], 1664). Kendall prepared thiacyanines by heating together 2-methylthiolbenzthiazole, alkyl *p*-toluenesulphonate, malonic acid and pyridine (B.P. 431141, 1933). The I.G. Farbenind. A.-G. prepared both symmetrical and unsymmetrical *thiacyanines* by condensing 3-alkylthiobenzthiazolone alkiodide with 2-methylbenzthiazole alkiodide in pyridine (B.P. 423792, 1932). Closely related is Kendall's method, in which a quaternary salt of 2-methylthiolbenzthiazole reacts with one of 2-methylbenzthiazole; he claims that it is advantageous to make the preparation and condensation of the salts all one process (B.P. 424559, 1933).



3:4:3′:4′-Bis-trimethylenethiacyanine iodide.
Bis-(3:4-trimethylene-2-benzthiazole)methincyanine iodide.
XII.

The *Thiacarbocyanines* (XI "*Thiazole Purple*") were prepared by König and Meier by condensing a 2-methylbenzthiazolium salt with ethyl orthoformate, or anhydrous sodium formate, in the presence of various solvents (J. pr. Chem. 1925, [ii], **109**, 324). Hamer found the ethyl orthoformate and pyridine method to be most successful in the case of the thiacarbocyanines (J.C.S. 1927, 2796), and subsequently condensed ethyl orthoformate, in the presence of pyridine, with salts of methyl-*α*- and *β*-naphthathiazoles (J.C.S. 1929, 2598), as also did Brooker and Kodak Ltd. (B.P. 354264; 359463, 1929). The I.G. Farbenind. A.-G. used ethyl orthoformate and pyridine in preparing thiacarbocyanines with complex nuclei (B.P. 396217, 1931) and in preparing certain substituted thiacarbocyanines (B.P. 418745; 420971, 1932; 421015, 1933), including those from methyltetrahydro-*α*- and *β*-naphthathiazoles (B.P. 427887, 1932) and from 2-methyl-*ββ*′-naphthathiazole (B.P. 452408, 1934). Kendall prepared thiacarbocyanines by heating together 2-methylthiolbenzthiazole, alko-*p*-toluene-sulphonate, crotonic anhydride, or glutaconic acid, and pyridine (B.P. 431141; 431186, 1933).

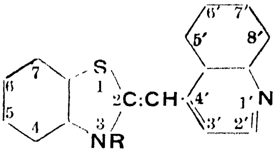
Mills and Braunholtz found that when the disulphide (IX) reacts with quinaldine ethonitrate, it behaves as explained under thiacyanines, so that the 2:2′-carbocyanine (V) is accompanied by the *thia-2′-cyanine* (XIII) (J.C.S. 1923, **123**, 2804). Hamer confirmed this formula by preparing thia-2′-cyanines by the action of caustic alkali on the alkiodides of 2-iodoquinoline and 2-methylbenzthiazole (*ibid.* 1928, 206), whilst more complex thia-2′-cyanines were prepared by using methyl-*α*- and *β*-naphthathiazole alkiodides and 2-iodo-*β*-naphthaquinoline alkiodide (*ibid.* 1929, 2598; Hamer and Kelly, *ibid.* 1931, 777). The I.G. Farbenind. A.-G. subsequently condensed 2-iodoquinoline alkiodide with salts of still more complex thiazole derivatives (B.P. 400401, 1931), of methyltetrahydro-*α*- and *β*-naphthathiazoles (B.P. 427887, 1932), and of 2-methyl-*ββ*′-naphthathiazole (B.P. 452408, 1934). They also prepared thia-2′-cyanines by the action of pyridine on a mixture of 1-ethyl-2-thioquinolone alkiodide and 2-methylbenzthiazole alkiodide, or of quinaldine alkiodide and 3-ethyl-2-nitrosomidobenzthiazoline (B.P. 423792, 1932). Ken-



3:1′-Dialkylthia-2′-cyanine iodide.
(1-*Alkyl-2-quinoline*)(3-*alkyl-2-benzthiazole*)*methincyanine iodide.*
XIII.

dall found it better to use alkyl-*p*-toluenesulphonates of the thione compounds (B.P. 438420, 1934); he also prepared thia-2'-cyanines by condensing salts of 1-methylthiolbenzthiazole and quinaldine (B.P. 424559, 1933). Beilenson and Hamer observed that introduction of chlorine or bromine atoms into the thia-, thiacarbo-, or thia-2'-cyanine molecule has little effect upon the absorption maximum (J.C.S. 1936, 1225).

Mills and Braunholtz found that when the disulphide (IX) reacts with lepidine ethonitrate, the 4:4'-carbocyanine (VIII) is accompanied by *thia-4'-cyanine* (XIV) (J.C.S. 1923, **123**, 2804), which they had previously obtained by the action of caustic alkali on the alkiodides of 2-methylbenzthiazole and quinoline (*ibid*. 1922, **121**, 2004). Brooker and Kodak Ltd. condensed quinoline alkiodide with alkiodides of methyl-α- and β-naphthathiazoles (B.P. 378455; 380140, 1930), whilst the I.-G. Farbenind. A.-G. used salts of still more complex thiazole derivatives (B.P. 400401, 1931), of methyltetrahydro-α- and β-naphthathiazoles (B.P. 427887, 1932), and of 2-methyl-ββ'-naphthathiazole (B.P. 452408, 1934). The I.G. Farbenind. A.-G. prepared thia-4'-cyanines by the action of pyridine and piperidine on alkiodides of lepidine and 3-methylthiobenzthiazolone (B.P. 423792, 1932), and Kendall prepared them by condensing quaternary salts of lepidine and 2-methylthiolbenzthiazole, or, conversely, of 4-methylthiolquinoline and 2-methylbenzthiazole (B.P. 424559, 1933).



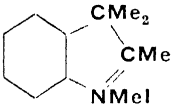
3:1'-Dialkylthia-4'-cyanine iodide.
(1-*Alkyl-4-quinoline*)(3-*alkyl-2-benzthiazole*)*methincyanine iodide*.
XIV.

Fuchs pointed out that certain sensitisers containing benzthiazole nuclei are superior to the older cyanines in that they inhibit chemical fog (Chem.-Ztg. 1933, **57**, 853); this is also confirmed by Sobolev, Bondareva and Evteeva, who compared the sensitising action of various substituted cyanines containing benz- and naphtha-thiazole nuclei (J. Appl. Chem. Russia, 1936, **9**, 335).

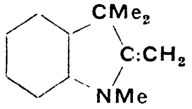
Other Cyanines and Symmetrical Carbocyanines.

Mills and Smith's discussion of the reactivity of the methyl group in heterocyclic bases (J.C.S. 1922, **121**, 2724) is of especial interest in connection with those bases which have since been found to give cyanine dyes. In the present section, the plan has been adopted of dealing, in roughly chronological order, with each base which was employed, on account of its reactive methyl group, for cyanine dye formation; this is followed by an account of further types made possible by methods depending on the reactivity of groups other than methyl.

Indocyanines, Indocarbocyanines, and Indo-2'-cyanines.—W. König pointed out that an indolenine salt such as (XV), can condense with ethyl orthoformate, in the presence of acetic anhydride, to give the *indocarbocyanine* (XVII) ("*Astraphloxine*") (Ber. 1924, **57**, 685), which method was subsequently used by Ghigi (Gazzetta, 1933, **63**, 698).

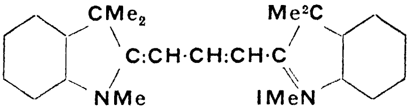


2:3:3-Trimethyl-indolenine methiodide.
XV.



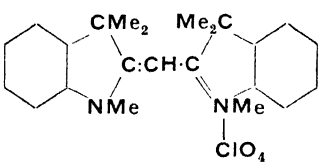
1:3:3-Trimethyl-2-methyleneindoline.
XVI.

Its sensitising properties were noted by Hamer, who prepared indocarbocyanines by use of ethyl orthoformate and pyridine (J.C.S. 1927, 2796).

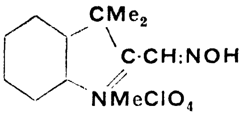


1:3:3:1':3':3'-Hexamethylindocarbocyanine iodide.
Bis-(1:3:3-*trimethyl-2-indolenine*)*trimethincyanine iodide*.
XVII.

They may also be prepared by condensation of the methylene base (XVI), which corresponds with (XV), with formaldehyde (Soc. Chem. Ind. in Basle, B.P. 312174, 1928). Kuhn and Winterstein prepared them by interaction of acetic anhydride, sodium formate, and a methylene base, or its salt with an organic acid (B.P. 328357, 1929). Ogata prepared (XVII) by treatment of (XV) with chloral hydrate and alkali (Proc. Imp. Acad. Tokyo, 1933, **9**, 602). Wahl and the I.G. Farbenind. A.-G. made "*Indolenine Yellow*" by treating salts such as (XV), or the corresponding base (XVI), with an ester or salt of nitrous acid, in the presence of acetic anhydride (G.P. 459616, 1926). Kuhn, Winterstein and Balser pointed out that neither the analytical results nor the colour of the compound accorded with the formula proposed, and they established that it is in fact the *indocyanine* (XVIII). By treating an acetic acid solution of (XVI) with sodium nitrite and then with perchloric acid, they isolated the oxime perchlorate (XIX), and showed that this reacts with



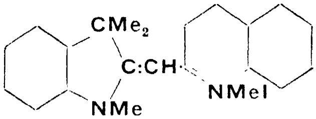
1:3:3:1':3':3'-Hexamethylindocyanine perchlorate.
Bis-(1:3:3-*trimethyl-2-indolenine*)*methincyanine perchlorate*.
XVIII.



3:3-Dimethyl-2-aldoxime-indolenine methoperchlorate.

XIX.

(XVI), in acetic anhydride solution, to give the indocyanine (XVIII); an *unsymmetrical indocyanine* was also prepared (Ber. 1930, **63**, [B], 3176). The intermediate (XIX) was also obtained by the action of nitrosyl chloride on (XV) or (XVI) (I.G. Farbenind. A.-G., B.P. 359753, 1929). Nitrosylsulphuric acid may be used similarly (I.C.I. Ltd., Linch, and Piggott, B.P. 391215, 1931). *Indo-2′-cyanines* (XX) were prepared by reaction of (XV) with 2-iodoquinoline alkiodide in the presence of caustic alkali (Hamer, J.C.S. 1928, 206), but triethylamine is recommended as a better condensing agent (Kodak, Ltd., B.P. 408571, 1932). With complex compounds of tungstic or molybdic acid, the indocyanines and indocarbocyanines give colour lakes which are fast to light, etc. (I.G. Farbenind. A.-G., B.P. 448508, 1934).



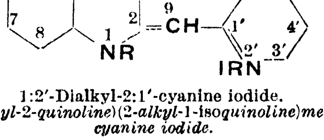
1:3:3·1′-Tetramethylindo-2′-cyanine iodide.
(1:3:3-*Trimethyl-2-indolenine*)(1-*methyl-2-quinoline*)-*methincyanine iodide*.

XX.

Oxacyanines, Oxacarbocyanines, Oxa-2′-cyanines, and Oxa-4′-cyanines.—König and Meier were the first to use 2-methylbenzoxazole methiodide for the preparation of a cyanine, condensing it with ethyl orthoformate and acetic anhydride to give an *oxacarbocyanine* (J. pr. Chem. 1925, [ii], **109**, 324). Hamer subsequently carried out the preparation by using ethyl orthoformate in conjunction with pyridine and noted that the oxacarbocyanines have photographic sensitising properties (J.C.S. 1927, 2796). Oxacarbocyanines were similarly prepared from methyl-α- and β-naphthoxazoles by Brooker and the Eastman Kodak Co. (U.S.P. 1939201, 1933; 1962123, 1934) and from 2-methyl-ββ′-naphthoxazole by the I.G. Farbenind. A.-G. (B.P. 432969, 1933). Kendall prepared oxacarbocyanines by reaction of the 2-methylthiolbenzoxazole alko-*p*-toluenesulphonates with glutaconic acid (B.P. 431141, 1933), or with crotonic anhydride, and pyridine (B.P. 431186, 1933). The colourless *oxacyanines* were prepared by Fisher and Hamer, by the action of amyl nitrite and acetic anhydride on salts of 2-methylbenzoxazole, and their pale yellow analogues were similarly prepared from methyl-α- and β-naphthoxazoles (J.C.S. 1934, 962). Kendall prepared oxacyanines by the action of malonic acid on a 2-methylthiolbenzoxazole alko-*p*-toluenesulphonate in pyridine (B.P. 431141, 1933), and was able to prepare both *symmetrical* and *unsymmetrical oxacyanines* by reaction of a 2-methylbenzoxazole quaternary salt with one of 2-methylthiolbenzoxazole (B.P. 424559, 1933) or of 3-alkyl-2-thiobenzoxazolone (B.P. 438420, 1934). The I.G. Farbenind. A.-G. obtained oxa-2′-cyanines by condensing quaternary salts of 2-methylbenzoxazole and 1-alkyl-2-thioquinolone (B.P. 423792, 1932; B.P. 423827, 1933) and patented oxa-2′- and *oxa-4′-cyanines* containing naphthoxazole nuclei (B.P. 388898, 1931; B.P. 432969, 1933). Kendall prepared oxa-2′-cyanines from salts of 2-methylthiolbenzoxazole and quinaldine (B.P. 424559, 1933). Brooker and Keyes found that, whereas the yield of oxa-2′-cyanine obtainable by the action of caustic alkali on an alcoholic solution of the ethiodides of 2-methylbenzoxazole and 2-iodoquinoline is very low, it can be greatly increased by using a strong organic base as condensing agent (J. Amer. Chem. Soc. 1935, **57**, 2488). The parent oxa-, oxacarbo-, oxa-2′-, and oxa-4′-cyanines are represented by formulæ (X), (XI), (XIII), and (XIV) respectively, if each sulphur atom be replaced by oxygen.

Selenacyanines, Selenacarbocyanines, Selena-2′-cyanines, and Selena-4′-cyanines.—Clark first used 2-methylbenzselenazole quaternary salts for the preparation of cyanines, and by their condensation with ethyl orthoformate and pyridine he prepared *selenacarbocyanines*, which he found to be sensitisers (J.C.S. 1928, 2313; *cf.* I.G. Farbenind. A.-G., B.P. 383486, 1931; 418745, 1932). From such salts or their derivatives, the I.G. Farbenind. A.-G. prepared, by the action of amyl nitrite and acetic anhydride, *selenacyanines* (B.P. 380702, 400951, 1931); by condensation with quinolinium salts, *selena-4′-cyanines* (B.P. 389969, 400951, 1931; *cf.* U.S.P. 2051134, 1936), and by condensation with a salt of 2-iodoquinoline or 1-alkyl-2-thioquinolone, *selena-2′-cyanines* (B.P. 386791, 400951, 1931; 403840, 423792, 1932). The parent selena-, selenacarbo-, selena-2′-, and selena-4′-cyanines may be represented by formulæ (X), (XI), (XIII), and (XIV) respectively, if each sulphur atom be replaced by selenium.

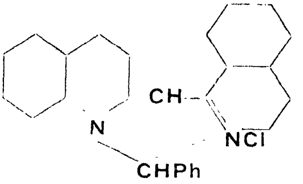
2:1′-Cyanines, 4:1′-Cyanines, Thia-1′-cyanines, and Selena-1′-cyanines.—Fisher and Hamer used 1-iodo*iso*quinoline alkiodide, in place of 2-iodoquinoline alkiodide, for cyanine condensations. Thus with quinaldinium salts in the presence of alcohol and alkali it gave *2:1′-cyanines* (XXI), which were also obtained, in much lower yield, by condensation of the alkiodides of *iso*quinoline and quinaldine. They pointed out that iso*Quinoline Red*, which had been prepared by interaction of *iso*quinoline, quinaldine, benzotrichloride, and zinc chloride



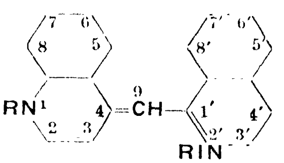
1:2′-Dialkyl-2:1′-cyanine iodide.
(1-*Alkyl-2-quinoline*)(2-*alkyl*-1-iso*quinoline*)*methincyanine iodide.*

XXI.

(Agfa, G.P. 40420, 1886) and formulated by Vongerichten and Homann as (XXII) (Ber. 1912, **45**, 3446; *cf.* Scheibe, Ber. 1921, **54**, [B], 786) is a 2:1′-cyanine of a special kind. 1-Iodo*iso*quinoline alkiodide was further condensed with lepidine alkiodide to give a 4:1′-*cyanine* (XXIII); with salts of 2-methylbenzthiazole, etc., to give *thia-1′-cyanines*; and with 2-methylbenzselenazole alkiodide to give a *selena-1′-cyanine*. Whereas the absorption maximum of each 1′-cyanine closely approximates to that of the analogous 2′-cyanine, the photographic sensitising action of the former is much weaker than that of the latter (J.C.S. 1934, 1905). Brooker and Keyes, by taking advantage of the reactive methyl group of salts of 9-methylphenanthridine, which may be considered as a derivative of both quinoline and *iso*quinoline, prepared four cyanines. In each instance the absorption maximum lay nearer the blue end of the spectrum than that of the isomeride containing a β-naphthaquinoline nucleus, whilst no sensitising action was shown (J. Amer. Chem. Soc. 1936, **58**, 659).

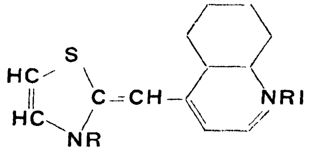


*iso*Quinoline Red.
1:2′-Benzylidene-2:1′-cyanine chloride.
1:2′*Benzylidene*(2-*quinoline*)(1′-iso*quinoline*)-*methincyanine chloride.*
XXII.



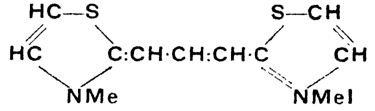
1:2′-Dialkyl-4.1′-cyanine iodide.
(1-*Alkyl-4-quinoline*)(2-*alkyl*-1-iso*quinoline*)-*methincyanine iodide.*
XXIII.

Thiazolocyanines, Thiazolocarbocyanines, Thiazolo-2′-cyanines, Thiazolo-1′-cyanines, Thiazolo-4′-cyanines, and Thiathiazolo-cyanines.—Mills and Smith pointed out the reactivity of the methyl group in a 2-methylthiazolium salt and, by condensing 4-phenyl-2-methylthiazole methiodide with quinoline methiodide, obtained the 4-phenyl derivative of the parent *thiazolo-4′-cyanine* (XXIV) (J.C.S. 1922, **121**, 2724; *cf.* I.G. Farbenind. A.-G., B.P. 386903, 1931).



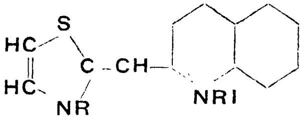
3:1′-Dialkylthiazolo-4′-cyanine iodide.
(3-*Alkyl-2-thiazole*)(1-*alkyl-4-quinoline*)*methincyanine iodide.*
XXIV.

From the same salt and the disulphide (IX) in pyridine, Mills and Braunholtz prepared the 4:4′-diphenyl derivative of the parent *thiazolocarbocyanine* (XXV) together with the corresponding *thiathiazolocyanine* (J.C.S. 1923, **123**, 2804).



3:3′-Dimethylthiazolocarbocyanine iodide.
Bis-(3-methyl-2-thiazole) trimethincyanine iodide.
XXV.

Fisher and Hamer prepared thiazolocarbocyanines from 2:4-dimethylthiazolium salts by the pyridine and ethyl orthoformate method (J.C.S. 1930, 2502). Brooker and Kodak Ltd. showed that, as prepared by the latter method, these are accompanied by the corresponding neocyanines (*q.v.*) (B.P. 408273, 1931). Kendall prepared a thiazolocarbocyanine from 2-methylthiolthiazolium *p*-toluenesulphonate and malonic acid in pyridine (B.P. 431141, 1933). *Thiazolo-2′-cyanines* (XXVI), prepared from 2-methylthiazolium and 2-iodoquinolinium salts, were described by Brooker, Keyes, and White (J. Amer. Chem. Soc. 1935, **57**, 2492; *cf.* Kodak Ltd., B.P. 408569; 408570, 1932; I.G. Farbenind. A.-G., B.P. 386903, 1931), and *thiazolo-1′-cyanines*, similarly prepared from 1-iodo*iso*quinolinium salts, were described by Fisher and Hamer (J.C.S. 1934, 1905).



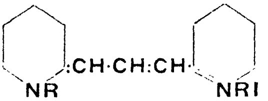
3:1′-Dialkylthiazolo-2′-cyanine iodide.
(3-*Alkyl-2-thiazole*)(1-*alkyl-2-quinoline*)*methincyanine iodide.*
XXVI.

Oxazolo- and Selenazolo-2′-cyanines.—By condensing 2-methyl-oxazolium or -selenazolium salts with 2-iodoquinolinium salts, Brooker, Keyes and White prepared *oxazolo-2′-cyanines* and a *selenazolo-2′-cyanine* (J. Amer. Chem. Soc. 1935, **57**, 2492). They may be represented by formula (XXVI), if the sulphur atom be replaced by oxygen and selenium respectively.

Thiazolinocarbocyanines, Thiazolino-2′-cyanines, and Thiazolino-4′-cyanines.—Quaternary salts of 2-methylthiazoline were first applied to cyanine formation by Brooker, who by condensation with ethyl orthoformate and pyridine obtained *thiazolinocarbocyanines*, with 2-iodoquinolinium salts obtained *thiazolino-2′-cyanines*, and with a quinolinium salt obtained a *thiazolino-4′-cyanine*, all of which are photographic sensitisers (J. Amer. Chem. Soc. 1936, **58**, 662). The formulæ of these three types resemble (XXV), (XXVI), and (XXIV) respectively, but the thiazoline nucleus in each instance takes the place of the thiazole nucleus. As compared with the corresponding dyes containing the thiazole nucleus, those with the thiazoline nucleus have their absorption maxima nearer to the region of short wave-length (Brooker, *l.c.*).

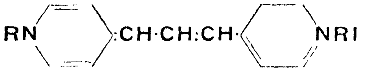
Selenazolinocarbocyanines.—White and Kodak Ltd. similarly used quaternary salts of 2-methylselenazoline to get *selenazolinocarbocyanines* (B.P. 392410; 406074, 1931). The formula resembles (XXV), but the selenazoline nucleus takes the place of the thiazole nucleus.

2:2′ and 2:4′-Pyridocarbocyanines, other Pyridocyanines, and Miscellaneous Cyanines.—Pyridocarbocyanines cannot be obtained from picolinium salts by the general methods used for other carbocyanines, but Rosenhauer and Barlet succeeded in preparing *2:2′-pyridocarbocyanines* (XXVII) by treating 2-picoline quaternary salts, in alcoholic solution, with potassium hydroxide and chloroform; by using a γ-picolinium salt, they prepared the *4:4′-pyridocarbocyanine* (XXVIII) (Ber. 1929, **62**, 2724). Ogata and Suzuki prepared (XXVII) by treating an α-picolinium salt with chloral hydrate and alkali (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 488). Hamer and Kelly were able to get *2-pyrido-2′-cyanines* (XXIX) by the action of caustic alkali on alkiodides of 2-iodopyridine and quinaldine, but not by the alternative method of using those of α-picoline and 2-iodoquinoline (J.C.S. 1931, 777). Brooker and Keyes, by employing triethylamine as condensing agent, however, were successful in preparing (XXIX) by the second method, and in improving its yield by the first method, and found this reagent superior to caustic alkali for 2′-cyanine preparations in general, and were thus enabled to make cyanines not previously accessible, such as *2-pyrido-4′-cyanine, 4-pyrido-2′-cyanine* (XXX), *2:2′-pyridocyanines* (XXXI), and *2:4′-pyridocyanines* (J. Amer. Chem. Soc. 1935, 57, 2488). Boilenson and Kodak Ltd. found potassium carbonate to be superior to caustic alkali for cyanine condensations (B.P. 435542, 1933). Brooker, Keyes and White used triethylamine in condensing 2-iodopyridinium salts with 2-methyl-thiazolium or -selenazolium salts, to give *2′-pyridothiazolocyanines* (XXXII) and *2′-pyridoselenazolocyanine* (XXXII, substituting **Se** for **S**) (J. Amer. Chem. Soc. 1935, **57**, 2492), whilst *2-′pyridothiazolinocyanines* are similarly obtainable (Brooker and Kodak Ltd., B.P. 437807, 1933). By condensing quaternary salts of α-picoline and 2-methylthiolbenzthiazole, Kendall prepared *2-pyridothiacyanine* (XXXIII) and this general method of applying a reactive methylthiol in conjunction with a methyl group was also applied to the preparation of *indothia-, indoxa-, oxaoxazolo-, oxathia-,* and *oxathiazolo-cyanines* (B.P. 424559, 1933). By condensing alkyl *p*-toluenesulphonates of 3-methylthiobenzoxazolone and α-picoline in pyridine, he prepared the *oxa-2′-pyridocyanine* (XXXIII, substituting **O** for **S**), and this method of using alkyl *p*-toluenesulphonates of a thione- and of a methyl- substituted base was also applied to some of the types mentioned above (B.P. 438420, 1934).



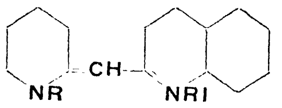
1:1′-Dialkyl-2:2′-pyridocarbocyanine iodide.
Bis-(1-alkyl-2-pyridine)trimethincyanine iodide.

XXVII.



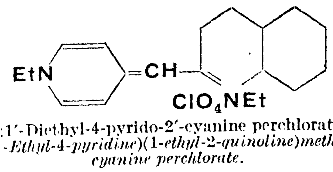
1:1′-Dialkyl-4:4′-pyridocarbocyanine iodide.
Bis-(1-alkyl-4-pyridine)trimethincyanine iodide.

XXVIII.



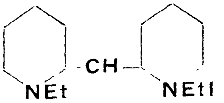
1:1′-Dialkyl-2-pyrido-2′-cyanine iodide.
(1-*Alkyl-2-pyridine*)(1-*alkyl-2-quinoline*)*methincyanine iodide.*

XXIX.



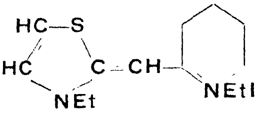
1:1′-Diethyl-4-pyrido-2′-cyanine perchlorate.
(1-*Ethyl-4-pyridine*)(1-*ethyl-2-quinoline*)*methincyanine perchlorate.*

XXX.



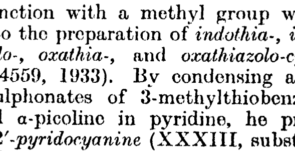
1:1′-Diethyl-2:2′-pyridocyanine iodide.
Bis-(1-ethyl-2-pyridine)methincyanine iodide.

XXXI.



3.1′-Diethyl-2′-pyridothiazolocyanine iodide.
(1-*Ethyl-2-pyridine*)(3-*ethyl-2-thiazole*)*methincyanine iodide.*

XXXII.



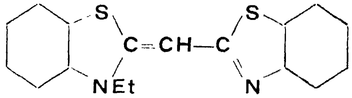
3:1′-Dialkyl-2′-pyridothiacyanine iodide.
(1-*Alkyl-2-pyridine*)(3-*alkyl-2-benzthiazole*)*methincyanine iodide.*

XXXIII.

(In naming unsymmetrical cyanines, other than those containing a quinoline or *iso*quinoline nucleus, confusion is avoided by using plain numerals to refer to the nucleus which is mentioned first, whilst the numerals with a dash refer to that which is mentioned second. It is convenient to arrange the prefixes in alphabetical order, *e.g.* indo- precedes oxa-, and oxa- precedes thia-.)

Of other nuclei which have been introduced into cyanines, Hamer, Heilbron, Reade and Walls first used the quinazoline nucleus, preparing a *quinazocarbocyanine* from a 2-methyl salt, ethyl orthoformate and pyridine (J.C.S. 1932, 251). Kendall, by taking advantage of reactive alkylthiol and methyl groups, prepared various types of cyanines containing one or two heterocyclic nuclei having two nitrogen atoms, such as quinazoline, pyrimidine and thiodiazole (B.P. 425609, 1933). By condensing the alkylthiol derivative of such an alko-*p*-toluenesulphonate with malonic acid in pyridine, he obtained symmetrical cyanines, in which two nuclei of this kind are linked by :CH· (B.P. 431141, 1933). With crotonic anhydride in pyridine a carbocyanine containing two thiodiazole nuclei was similarly prepared (B.P. 431186, 1933). Ogata described a carbocyanine containing two benziminazole nuclei as being prepared from 1:2-dimethylbenziminazole methiodide, diphenylformamidine, potassium acetate, and acetic anhydride (Proc. Imp. Acad. Tokyo, 1933, **9**, 602).

Bases, of which Cyanines are the Quaternary Salts.—Mills synthesised the ethiodide of dibenzthiazolylmethane, which, by elimination of acid, gave the base (XXXIV), of which



3′-Ethylbenzthiazolenyl-2-benzthiazolylmethane.

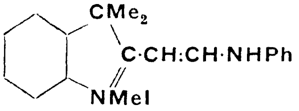
XXXIV.

(X) is the ethiodide (J.C.S. 1922, **121**, 455). Clark, from 2-imino-3-methylbenzthiazoline and quinaldine, prepared the base, of which thia-2′-cyanine (XIII) is the alkiodide (J.C.S. 1936, 507). Kendall patented a series of such bases, including those of which 2:2′-, oxa-2′-, selena-2′-, thia-2′- and thia-4′-cyanines also indo-2′-carbocyanine, are the quaternary salts, the method being to condense a base, having a reactive methyl group, with a quaternary salt, having a reactive alkylthiol, or substituted aminovinge group ; the resultant bases sensitise differently from, and sometimes more powerfully than, the corresponding salts (B.P. 456362, 1935).

Unsymmetrical Carbocyanines.—The methods which have been described so far for preparing carbocyanines lead of necessity to products in which the two heterocyclic nuclei are identical. It is true that mixtures of two quaternary salts may be used, as in the preparation of 2:4′-carbocyanines, but in this case the desired product must be separated from the isomerides which accompany it. Apart from this, Mills and Raper were the first to prepare unsymmetrical 2:2′-carbocyanines, by heating the methylene base from quinaldine ethiodide with a substituted quinaldinium salt and formaldehyde in alcoholic solution (J.C.S. 1925, **127**, 2466). The Society of Chemical Industry in Basle claimed that by condensing 1 mol. of a compound X·CH:NH (*e.g.* formimino ethyl ether hydrochloride) with 2 mols. of a heterocyclic ammonium salt containing a reactive methyl group, or with the corresponding pseudo-base, symmetrical carbocyanines result, whilst equimolecular quantities give an intermediate, which may subsequently be condensed with a second mol. of methylene base to give an unsymmetrical carbocyanine. Examples are the intermediate prepared from (XVI), also those from certain quinaldinium salts ; the first of these may be condensed with a second mol. of (XVI) to give (XVII), or with a different methylene base to give an unsymmetrical carbocyanine (B.P. 334706, 1928). I.C.I. Ltd., Piggott, and Rodd similarly used diarylformamidines, ArNH·CH:NAr, to get either symmetrical carbocyanines (when 2 mols. of quaternary salt containing a reactive methyl group are treated with one of

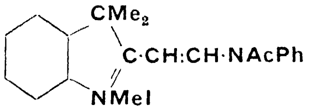
ArNH·CH:NAr),

or intermediates (when equimolecular proportions react). Thus (XV) heated with diphenylformamidine gives (XXXV), whilst in the presence of acetic anhydride its acetyl derivative (XXXVI) is produced (B.P. 344409, 1929).



2-ω-Anilinovinyl-3:3-dimethylindolenine methiodide.

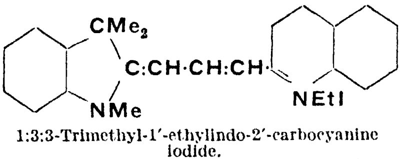
XXXV.



2-ω-Acetanilidovinyl-3:3-dimethylindolenine methiodide.

XXXVI.

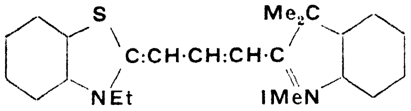
They found that such intermediates, by heating with acetic anhydride, potassium acetate, and a second mol. of heterocyclic ammonium salt containing a reactive methyl group, give carbocyanines, for example, the intermediate from diphenylformamidine and quinaldine ethiodide gives with (XVI) the unsymmetrical *indo-2′-carbocyanine* (XXXVII) ; that derived from 2-methylbenzthiazole ethiodide gives with (XV) the *indothiacarbocyanine* (XXXVIII); (XXXVI) with 2-methylbenzoxazole ethiodide gives the *indoxacarbocyanine* (XXXIX) ; and the intermediate derived from 2-methylbenzthiazole ethiodide gives with 2-methylbenzoxazole ethiodide the *oxathiacarbocyanine* (XL) ; these four dyes are photographic sensitisers (B.P.



1:3:3-Trimethyl-1′-ethylindo-2′-carbocyanine iodide.

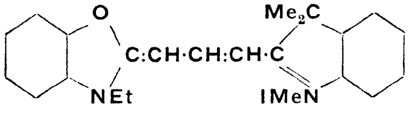
(1:3:3-*Trimethyl-2-indolenine*)(1-*ethyl-2-quinoline*)-*trimethincyanine iodide.*

XXXVII.



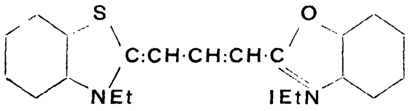
1:3:3-Trimethyl-3′-ethylindothiacarbocyanine iodide.
(1:3:3-*Trimethyl-2-indolenine*)(3-*ethyl-2-benzthiazole*)-*trimethincyanine iodide*.

XXXVIII.



1:3:3-Trimethyl-3′-ethylindoxacarbocyanine iodide.
(1:3:3-*Trimethyl-2-indolenine*)(3-*ethyl-2-benzoxazole*)-*trimethincyanine iodide*.

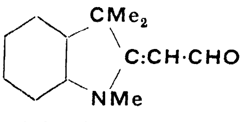
XXXIX.



3:3′-Diethyloxathiacarbocyanine iodide.
(3-*Ethyl-2-benzoxazole*)(3-*ethyl-2-benzthiazole*)-*trimethincyanine iodide*.

XL.

354898, 1930). Ogata applied their method to the preparation of various carbocyanines and demonstrated the virtual tautomerism of this series; whereas the dye prepared from a quaternary salt A and the intermediate from a salt B is identical with that prepared from the salt B and the intermediate from A, the yields may be different. He obtained better results with the acetanilido- than with the anilino-intermediate. By use of dimethylquinoline, etc., he prepared carbocyanines with an extra methyl group, which was subsequently caused to react with *p*-dimethylaminobenzaldehyde (Proc. Imp. Acad. Tokyo, 1932, **8**, 119; Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 501, 519, 549, 556). In preparing an *indoquinazocarbocyanine*, Kendall used pyridine, in place of acetic anhydride and potassium acetate (B.P. 425609, 1933). The I.G. Farbenind. A.-G. states that indoxacarbocyanines are especially good sensitisers (B.P. 442160, 1933). To prepare carbocyanines containing an indolenine nucleus, they condensed an aldehyde, such as (XLI)

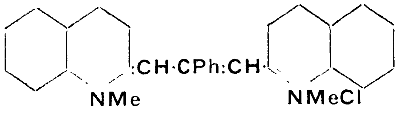


1:3:3-Trimethylindoline-2-methylene-ω-aldehyde.

XLI.

(B.P 438278, 1933), with a quaternary salt containing a reactive methyl group (or with the corresponding methylene base), in the presence of a solvent and condensing agent (B.P. 438603, 1933).

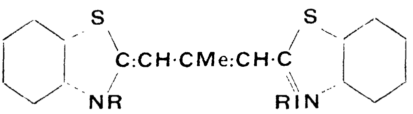
Cyanines with Substituents on the Chain.—The first recorded instance of a cyanine substituted on the chain is the dinitro- derivative which Mills and Hamer obtained by treating 2:2′-carbocyanine with nitric acid (J.C.S. 1920, **117**, 1550; Hamer, *ibid.* 1928, 3160), and the second is *neocyanine*, which will be dealt with in a later section. A direct synthesis of the 10-phenyl-2:2′-carbocyanine (XLII) was



10-Phenyl-1:1′-dimethyl-2:2′-carbocyanine chloride.
Bis-(1-*methyl-2-quinoline*)β-*phenyltrimethincyanine chloride*.

XLII.

effected by Fischer and Rosenhauer (Z. angew. Chem. 1923, **36**, 330), and by Rosenhauer, Schmidt and Unger (Ber. 1926, **59**, 2356), by heating the methylene base from quinaldine methomethylsulphate with benzotrichloride in alcoholic solution (*cf.* Ogata and Suzuki, Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 479). Hamer, by heating quaternary salts containing a reactive methyl group with ethyl orthoacetate in the presence of pyridine, succeeded in preparing 9-*methylthiacarbocyanines* (XLIII), the results

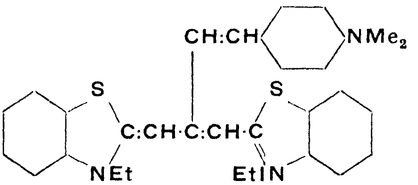


9-Methyl-3:3′-dialkylthiacarbocyanine iodide.
Bis-(3-*alkyl-2-benzthiazole*)β-*methyltrimethincyanine iodide*.

XLIII.

being negative with other types of heterocyclic bases (J.C.S. 1928, 3160). Subsequently 9-methylthiacarbocyanines were obtained from 1-methyl-α- but not from 2-methyl-β-naphthathiazolium iodides (*ibid.* 1929, 2598). Brooker and White, however, obtained a 9-methylthiacarbocyanine from 2-methyl-β-naphthathiazole, by using the etho-*p*-toluenesulphonate instead of the ethiodide of the base. They prepared 9-*methylselenacarbocyanine* and 9-*methyloxacarbocyanine* by use of a 2-methylbenzoxazolium iodide, ethyl orthoacetate, and triethylamine in pyridine solution. They observed that 9-methylthiacarbocyanine is formed on heating a 2-methylbenzthiazolium salt with pyridine only, and that this same method is applicable to salts of methyl-α- and β-naphthathiazoles, 2-methylbenzselenazole, and 2-methylbenzoxazole (J. Amer. Chem. Soc. 1935, **57**, 547). By condensing 1-methylbenzthiazolium salts in the presence of pyridine with various ortho-esters, they prepared thiacarbocyanines in which the central carbon atom of the chain carried an alkyl, aryl, or aralkyl group. 9-*Ethyl*- and 9-*phenyl-selenacarbocyanine* and 9-*ethyl-oxacarbocyanine* were also described (J. Amer. Chem. Soc. 1935, **57**, 2480). White and Kodak Ltd. prepared 7-*ethylselenazolinocarbocyanines* (B.P. 392410, 1931), and Brooker prepared 7-*ethylthiazolinocarbocyanines* (J. Amer. Chem. Soc. 1936, **58**, 662). Arranging the thiacarbocyanines in order of increasing wavelength of absorption maximum, Brooker and White found the 9-substituents to fall in the order **Me**, **Et**, **H**, **Ph**, and the 4:5:′4:5′- and 6:7:6′:7′-dibenzthiacarbocyanines and selenacarbocyanines were similar, but the oxacarbocyanines abnormal (J. Amer. Chem. Soc. 1935, **57**, 2480); the same order was later found for 6:6′-dichloro- or -dibromo- substituted thiacarbocyanines (Beilenson and Hamer, J.C.S. 1936, 1225). The I.G. Farbenind. A.-G. has patented *meso*-substituted oxa-, selena-, or thia-carbocyanines, which are variants of those described above, through having either more complex nuclei or nuclei carrying substituents (B.P. 396217; 402458; 410481, 1931; 415949, 1933; 418745; 420971; 421015; 427887, 1932; 432969, 1933; 452408, 1934). Although they have patented dyes prepared by the action of carbon tetrahalogenide on a methylene base derived from a methyl-indoleninium salt (*e.g.* (XVI), derived from (XV)), or from the corresponding 2-methylbenzthiazolium or quinaldinium salts, no formula is given (B.P. 373160, 1931). Kendall and Ilford Ltd. patented the preparation of *meso*-substituted carbocyanines by using an imino-ether, **R′O·CR:NH**, instead of an ortho-ester (B.P. 404997, 1932); also by condensing a quaternary salt, containing a reactive methyl group, with an acid anhydride, in the presence of an acid-binding agent (B.P. 369236, 1930).

Ogata found the 9-methyl group of thiacarbocyanines to be reactive: by treatment of a 9-methylthiacarbocyanine with furfuraldehyde, benzaldehyde, or *p*-dimethylaminobenzaldehyde in the presence of alcohol and piperidine, he prepared the corresponding 9-furylvinyl-, 9-styryl-, or 9-*p*-dimethylaminostyrylthiacarbocyanine (XLIV) (Bull. Chem. Soc. Japan, 1936, **11**, 262).



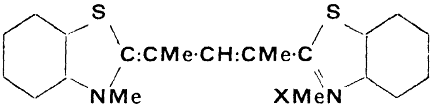
3:3′-Diethyl-9-*p*-dimethylaminostyrylthiacarbocyanine iodide.
Bis-(3-*ethyl*-2-*benzthiazole*)β-*p*-*dimethylaminostyryltrimethincyanine iodide.*

XLIV.

By making use of the ortho-ester of thiophen-α-carboxylic acid, the I.G. Farbenind. A.-G. prepared carbocyanines with an α-thienyl group in the *meso*-position (B.P. 403845, 1932). They also introduced, into this position, groups such as *cyclo*hexyl-, furyl-, or pentadecyl-, by treating a benzoxazolium salt, containing the desired group in the 2-position, with sodium ethoxide in alcohol, followed by a quaternary salt containing a reactive methyl group (B.P. 439359, 1933). By means of ortho-esters, $RS\cdot CH_2\cdot C(OEt)_3$, the $RS\cdot CH_2\cdot$ group was introduced into the 9-position of thiacarbocyanines, but neither this nor the introduction of alkylthiol groups into the rings improved either the photographic sensitising or the stabilising action of the parent dyes (Kiprianov, Suitnikov and Suitsch, J. Gen. Chem. Russ. 1936, **6**, 576).

The foregoing methods lead to *meso*-substituted symmetrical carbocyanines, but the I.G. Farbenind. A.-G., by utilising the alkyl ester of an arylated thioimide, **ArN:CR·SR′**, prepared unsymmetrical carbocyanines with the substituent **R** in the *meso*-position (B.P. 412309, 1932).

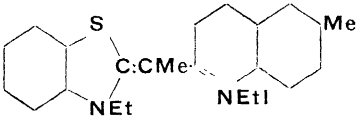
König, Kleist and Götze, by condensing 2-ethylbenzthiazole methiodide with ethyl orthoformate, isolated a thiacarbocyanine (XLV), in which the two lateral carbon atoms of the chain bear substituents (Ber. 1931, **64**, 1664).



3:8:10:3′-Tetramethylthiacarbocyanine salt.
Bis-(3-*methyl*-2-*benzthiazole*)αγ-*dimethyltrimethincyanine salt.*

XLV.

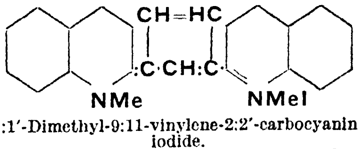
The I.G. Farbenind. A.-G. applied such quaternary salts, in which the reactive methyl group is replaced by $—CH_2R$, to the preparation of other symmetrical and unsymmetrical carbocyanines with one or more **R** groups in the α-position in the chain (B.P. 405309; 411876, 1931), and also to obtaining 2′-cyanines, *e.g.* XLVI, in which the nuclei are linked by **:CMe·** (B.P. 405309, 1931; 423792, 1932). Götze, however, reported that when ethiodides of 2-ethylbenzthiazole and 2-iodoquinoline are treated with alkali, the 2′-cyanine is accompanied by an unknown dye (Angew. Chem. 1936, **49**, 563).



8:6′-Dimethyl-3:1′-diethylthia-2′-cyanine iodide.
(6-*Methyl*-1-*ethyl*-2-*quinoline*)(3-*ethyl*-2-*benzthiazole*)-*methylmethincyanine iodide.*

XLVI.

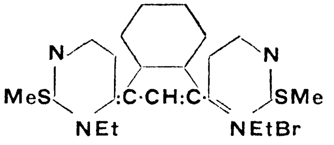
By heating the alko-*p*-toluenesulphonate of a base containing an alkylthiol group (or, alternatively, the isomeric thione) with *cyclo*pentadiene and pyridine, Kendall prepared carbocyanines in which the three-carbon chain, joining the heterocyclic nuclei, itself forms part of a *cyclo*pentadiene nucleus. The method was applied to the preparation of carbocyanines from dimethylthiolthio-ββ′-diazole, and of 2:2′-carbocyanines (*e.g.* XLVII), as well as of oxa- and thia-



1:1′-Dimethyl-9:11-vinylene-2:2′-carbocyanine iodide.
Bis-(1-*methyl*-2-*quinoline*)αγ-*vinylenetrimethincyanine iodide.*

XLVII.

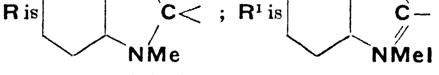
carbocyanines. By using indene instead of *cyclo*pentadiene, an *o*-phenylene group may be introduced instead of vinylene, and this has been done with oxa-, thia-, 2:2′-, 2:2′-pyrido, quinazo-, and 4:4′-pyrimido-carbocyanines (*e.g.* XLVIII), besides others containing two thio-ββ′- or thio-αβ′-diazole nuclei. According to the nature of the nuclei, the compounds sensitise, or even desensitise, chloride or bromide emulsions; the cyclisation of the chain has a hypsochromic effect (B.P. 431142; 431187, 1933).



2:2′-Dimethylthiol-1:1′-diethyl-5:7-*o*-phenylene-6:6′-pyrimidocarbocyanine bromide.
Bis-(2-methylthiol-1-ethyl-6-pyrimidine)αγ-o-phenylene-trimethincyanine bromide.
XLVIII.

Dicarbocyanines.—Beattie, Heilbron and Irving condensed a heterocyclic ammonium salt containing a reactive methyl group (or the corresponding methylene base) with derivatives of bromo-, chloro- or nitro-malondialdehyde, or a suitable acraldehyde derivative, *e.g.* the anil of α-bromo-β-anilinoacraldehyde, PhN:CH·CBr:CH·NHPh, either in pyridine in the presence of piperidine, or in acetic anhydride in the presence of potassium acetate; they thus prepared cyanines in which the two heterocyclic nuclei are linked by a five-carbon chain, the central carbon atom of which carries as substituent Br, Cl, or NO_2. As cyanines with a three-carbon chain had been designated "carbocyanines," these new dyes were called "dicarbocyanines." By using alkiodides of quinaldine, lepidine, 2-methylbenzthiazole, 2:3:3-trimethylindolenine, and 2-methylbenzoxazole, there were obtained, respectively, meso-*substituted*-2:2′-, 4:4′-*thia-*, *indo-*, and *oxa-dicarbocyanines* (*e.g.* XLIX).

R:CH·CH:C(NO_2)CH:CH·R¹



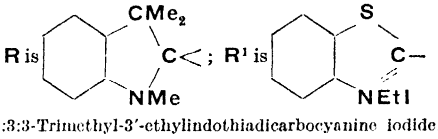
10-Nitro-1:3:3:1′:3′:3′-hexamethylindodicarbocyanine iodide.
Bis-(1:3:3-trimethyl-2-indolenine)γ-nitropentamethincyanine iodide.
XLIX.

They found that whilst the halogenodicarbocyanines are sensitisers for the deep red or near infra-red, the corresponding nitrodicarbocyanines possess desensitising properties (J.C.S. 1932, 260; *cf.* I.C.I. Ltd., Heilbron, and Irving, B.P. 353889, 1930). By the action of β-anilinoacraldehyde anil,

PhNH·CH:CH·CH:NPh,

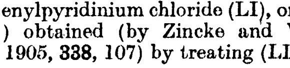
in acetic anhydride, on an equimolecular quantity of a salt such as (XV), I.C.I. Ltd., Piggott, and Rodd isolated an intermediate compound, which, by condensation with a heterocyclic ammonium salt containing a reactive methyl group, gave a dicarbocyanine with an unsubstituted five-carbon chain. Where the two quaternary salts are the same, the resultant dye is symmetrical, where they differ it is unsymmetrical: *e.g.* the intermediate from (XV) with 1-methylbenzthiazole ethiodide gave (L), or, alternatively, this was prepared from the intermediate obtained from 2-methylbenzthiazole ethiodide, together with (XVI) (B.P. 355693, 1930). For preparing dicarbocyanine intermediates, the I.G. Farbenind. A.-G. found it advantageous to use an organic base, in alcohol, as condensing agent; they recorded the absorption maxima of many such intermediates, and the sensitising and absorption maxima of various types of *unsymmetrical dicarbocyanines* prepared from them (B.P. 434234; 434235, 1933). They have patented various substituted dicarbocyanines, including dyes carrying one or more methyl groups on the chain (B.P. 388204; 394537, 1931; 427887, 1932; 452408, 1934) and others are described by Beilenson and Hamer (J.C.S. 1936, 1225). Kendall and Ilford Ltd. used propargylaldehyde acetal, or its derivatives, for condensing with quaternary salts containing reactive methyl groups, to furnish the three central carbon atoms of the dicarbocyanine chain (B.P. 390808, 1931), and prepared a thiadicarbocyanine by heating 2-methylthiolbenzthiazole metho-*p*-toluenesulphonate with sorbic anhydride in the presence of pyridine (B.P. 431186, 1933). In Ogata's preparation of dicarbocyanines by heating a carbocyanine intermediate, *e.g.* (XXXV), and a quaternary salt (XV), with orthoformic ester and acetic anhydride, the course of the reaction is not clear (Proc. Imp. Acad. Tokyo, 1934, **10**, 572).

R:CH·CH:CH·CH:CH·R¹

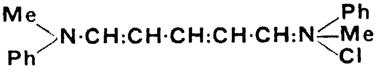


1:3:3-Trimethyl-3′-ethylindothiadicarbocyanine iodide.
(1:3:3-*Trimethyl-2-indolenine*)(3-*ethyl-2-benzthiazole*)-*pentamethincyanine iodide.*
L.

Tricarbocyanines.—Tricarbocyanines, in which the nuclei are linked by a seven-carbon chain, were described by three sets of workers. Wahl and the I.G. Farbenind. A.-G. condensed (XV) or (XVI) with (*a*) a compound such as 2:4-dinitrophenylpyridinium chloride (LI), or (*b*) the dye (LII) obtained (by Zincke and Würker, Annalen, 1905, **338**, 107) by treating (LI) with a



2:4-Dinitrophenylpyridinium chloride.
LI.


$$\mathrm{\overset{Me}{\underset{Ph}{>}}N{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}N\overset{Ph}{\underset{Cl}{<}}Me}$$

5-Methylanilino-1-phenyliminomethochloride-$\Delta^{2:4}$-pentadiene.

LII.

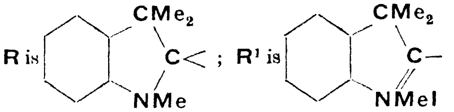
base such as methylaniline. With equimolecular proportions, in acetic anhydride, (LIII) resulted. But 2 mols. of quaternary salt to 1 mol. of (LI) or (LII) gave the *indotricarbocyanine* (LIV) (G.P. 499967, 1928).

$\mathrm{MePhN{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}R^1}$

6-Methylanilino-$\Delta^{1:3:5}$-hexatriene-3′:3′-dimethylindolenyl methiodide.

LIII.

$\mathrm{R{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}R^1}$

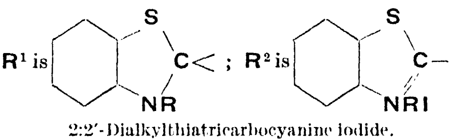


1·3:3:1′:3′:3′-Hexamethylindotricarbocyanine iodide. *Bis-*(1:3:3-*trimethyl-2-indolenine*)*heptamethincyanine iodide.*

LIV.

I.C.I. Ltd., Piggott, and Rodd also condensed (XVI) with a compound of type (LII) to give (LIV), which they observed to be a sensitiser for infra-red light (B.P. 355693, 1930). Fisher and Hamer prepared dyes by use of (LI) or a compound of a type similar to (LII), preferably the latter, carrying out the reaction in alcoholic solution in the presence of caustic alkali; the generality of the method, in that various quaternary ammonium salts containing a reactive methyl group are applicable, was pointed out, and the sensitising properties for infra-red light were noted. There were prepared *thiatricarbocyanines* (LV), including those containing α- and β-naphthathiazole nuclei, *selenatricarbocyanines* (as LV, but Se for S), *thiazolinotricarbocyanines*, and 2:2′-*tricarbocyanines* (LVI).

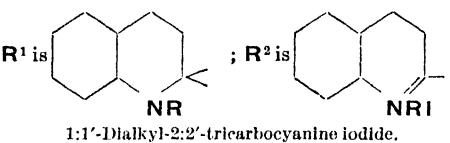
$\mathrm{R^1{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}R^2}$



2:2′-Dialkylthiatricarbocyanine iodide. *Bis-*(2-*alkyl-*1-*benzthiazole*)*heptamethincyanine iodide.*

LV.

$\mathrm{R^1{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}R^2}$

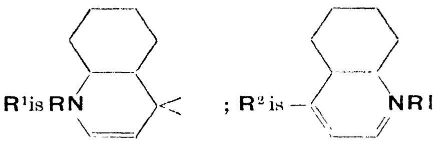


1:1′-Dialkyl-2:2′-tricarbocyanine iodide. *Bis-*(1-*alkyl-*2-*quinoline*)*heptamethincyanine iodide.*

LVI.

The indotricarbocyanine (LIV) was obtained by use of acetic anhydride and sodium acetate (J.C.S. 1933, 189). Brooker and Kodak Ltd., by using triethylamine, etc., instead of caustic alkali, for condensing an intermediate of type (LII) with the appropriate quaternary salt, succeeded in preparing *thiazolotricarbocyanines* and 4:4′-*tricarbocyanines* (*Xenocyanine*) (LVII) (B.P. 436941; 437017, 1933).

$\mathrm{R^1{\cdot}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}R^2}$



1:1′-Dialkyl-4:4′-tricarbocyanine iodide. *Bis-*(1-*alkyl-*4-*quinoline*)*heptamethincyanine iodide.*

LVII.

Brooker, Hamer and Mees published spectrograms illustrating the sensitising action of tricarbocyanines (Phot. J. 1933, **73**, 258); as did also Dieterle, Dürr and Zeh, who pointed out that various types of di- and tri-carbocyanines had been independently prepared in Germany, chiefly owing to the work of König, and put into commercial use (Z. wiss. Phot. 1933, **32**, 145). Certain more complex, or substituted, tricarbocyanines have been described (I.G. Farbenind. A.-G., B.P. 388204, 1931; 452408, 1934; Beilenson and Hamer, J.C.S. 1936, 1225). As a tricarbocyanine intermediate, Kendall found 2-benzoxazolylpyridinium chloride, prepared from 2-chlorobenzoxazole and pyridine, to be preferable to (LI) (B.P. 424264, 1933). Brooker and Kodak Ltd. patented the preparation of tricarbocyanines by interaction of a quaternary heterocyclic ammonium salt, containing a reactive methyl group, with an alkiodide of 2-iodo-pyridine or -quinoline, in pyridine solution (B.P. 435252, 1933).

By making use of an intermediate, similar to (LII), but prepared from a suitably substituted pyridinium salt, the I.G. Farbenind. A.-G. synthesised tricarbocyanines carrying a methyl group on the chain (B.P. 394537, 1931). Corbellini and Fusco halogenated anils of type (LII) and used these to make tricarbocyanines with a halogen atom on the chain, and found these dyes to be as good sensitisers as the parent dyes (Rend. Ist. Lomb. Sci. Lett. 1935, [ii], **68**, 961). Dieterle and Zeh record, on the other hand, that tricarbocyanines carrying a γ-acetoxy group on the chain (I.G. Farbenind. A.-G., B.P. 441624, 1933) (*see also under* tetra- and penta-carbocyanines) are less good sensitisers than the unsubstituted compounds (Z. wiss. Phot. 1935, **34**, 245). To prepare tricarbocyanine intermediates, similar to (LIII), the I.G. Farbenind. A.-G. found an alkaline medium advantageous; they recorded the absorption maxima of several such intermediates, and the sensitising action of various *unsymmetrical tricarbocyanines* prepared from them (B.P. 438449; 438450; 438484, 1933).

Comparisons of Series.—In the *indo-* series, Kuhn and Winterstein found that the tricarbocyanine is the most easily reduced, the dicarbocyanine less readily, and the carbocyanine still less readily, the cyanine being the most resistant (Ber. 1932, **65**, [B], 1737). In the 2:2′-, 4:4′-

indo-, oxa-, pyrido-, thia-, thiazolino- and thiazolo- series, Ogata tabulated the melting-point of the corresponding carbo-, dicarbo- and tricarbo-cyanine, and the sensitising maximum of each ; he found the latter to be shifted regularly towards the red on lengthening the polymethin chain. He also compared the yields when corresponding carbo-, dicarbo- and tricarbo-cyanines are prepared by use of the appropriate anil in an acid or alkaline medium respectively (Proc. Imp. Acad. Tokyo, 1932, **8**, 421 ; 1933, **9**, 602 ; Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 528 ; Ogata and Kimura, *ibid.* 1934, **13**, 537). The optical and photographic properties of typical cyanines were studied by Bloch and Hamer (Phot. J. 1928, **68**, 21 ; 1930, **70**, 374). Fisher and Hamer compared the frequencies of maximum absorption of methyl alcoholic solutions of the cyanine, carbo-, dicarbo- and tricarbo-cyanine of various symmetrical types, correlating frequency changes with changes in chemical constitution ; *e.g.* the values of the frequency-decreases, caused by each successive lengthening of the chain joining the nuclei, became smaller with increasing length of chain (Proc. Roy. Soc. 1936, A, **154**, 703).

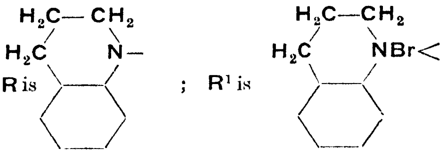
Tetra- and *Penta-carbocyanines.*—Somewhat as the pyridinium nucleus of (LI) had been ruptured to give the open-chain compound (LII), so König had ruptured the furfural nucleus, by treatment with an aromatic base, to give (*e.g.*) (LVIII) (J. pr. Chem. 1905, (ii), **72**, 555) and that of furylacrolein to give (*e.g.*) (LIX) ($n=1$) (*ibid.* 1913, (ii), **88**, 193).

$$[PhNH\cdot CH{:}CH\cdot CH{:}C(OH)CH{:}NPh]HBr$$

α-Hydroxyglutaconaldehyde dianilide hydrobromide.

LVIII.

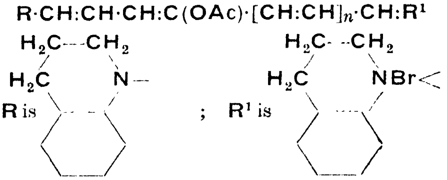
$$R\cdot CH{:}CH\cdot CH{:}C(OH)\cdot[CH{:}CH]_n\cdot CH{:}R^1$$



LIX.

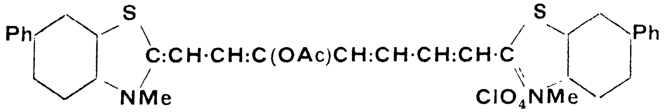
Subsequently, König (with Hey, Schulze, Silberkweit and Trautmann) prepared corresponding dyes with nine- and eleven-membered carbon-chains (LIX, $n=2$ and 3, respectively), by rupture of the nuclei of 5-furyl-$\Delta^{2:4}$-pentadiene-1-al and 7-furyl-$\Delta^{2:4:6}$-heptatriene-1-al respectively. These dyes are unstable, the instability increasing as the chain is lengthened. By acylation (or benzoylation), with an acid anhydride or chloride in the presence of pyridine, the stability is, however, increased : the preparation of compounds such as (LX) (where $n=$ 0, 1, 2 or 3) made possible the preparation of

$$R\cdot CH{:}CH\cdot CH{:}C(OAc)\cdot[CH{:}CH]_n\cdot CH{:}R^1$$



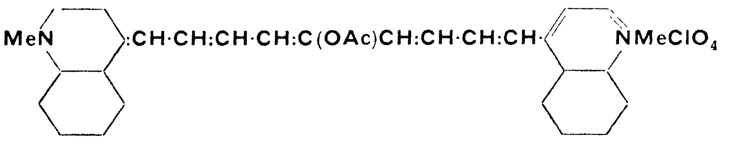
LX.

cyanines in which the nuclei are joined by longer chains (Ber. 1934, **67**, [B], 1274). The I.G. Farbenind. A.-G. has patented such cyanines, with a chain of at least seven carbon atoms, and describes them as excellent sensitisers to infra-red light ; the examples include 10-acetoxythia-



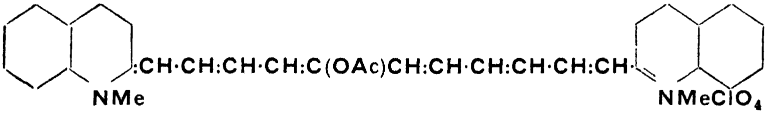
10-Acetoxy-6:6′-diphenyl-3:3′-dimethylthiatricarbocyanine perchlorate.
Bis-(6-phenyl-3-methyl-2-benzthiazole)γ-acetoxyheptamethincyanine perchlorate.

LXI.



13-Acetoxy-1:1′-dimethyl-4:4′-tetracarbocyanine perchlorate.
Bis-(1-methyl-4-quinoline)ε-acetoxynonamethincyanine perchlorate.

LXII.



13-Acetoxy-1:1′-dimethyl-2:2′-pentacarbocyanine perchlorate.
Bis-(1-methyl-2-quinoline)ε-acetoxyundecamethincyanine perchlorate.

LXIII.

tricarbocyanines (*e.g.* LXI), 12-acetoxy- (or 12-benzoxy-) thiatetracarbocyanines and the corresponding acetoxy- indo-, selena-, and 4:4′-tetracarbocyanines (*e.g.* LXII), also 11-acetoxy-thia- and 13-acetoxy-2:2′-pentacarbocyanines (*e.g.* LXIII) (B.P. 441624, 1933).

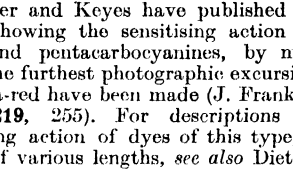
Brooker and Keyes have published spectrograms showing the sensitising action of such tetra- and pentacarbocyanines, by means of which the furthest photographic excursions into the infra-red have been made (J. Franklin Inst. 1935, **219**, 255). For descriptions of the sensitising action of dyes of this type, having chains of various lengths, *see also* Dieterle and Zeh (Z. wiss. Phot. 1935, **34**, 245).

More recently Dieterle and Riester have succeeded in synthesising tetra- and pentacarbocyanines not substituted in the chain; these are more powerful sensitisers than their acetoxy-substituted derivatives (Z. wiss. Phot. 1937, **36**, 68, 141).

apo*Cyanines*.—By heating quinoline alkiodide with caustic alkali in alcoholic solution, Kaufmann and Strübin obtained as chief product a red compound, *erythro*apo*cyanine*, together with some yellow compound, *xantho*apo*cyanine*; these were unlike the other cyanines then known, in being more stable to acid (Ber. 1911, **44**, 690; *cf.* G.P. 154448, 1903). König formulated them as (LXIV) and (LXV) respectively, but without giving any evidence (Ber. 1922, **55**, [B], 3293). The formulæ were, however, proved to be correct by Mills and Ordish, who, by the action of potassium permanganate on the erythro*apo*cyanine from quinoline ethiodide, obtained the same oxidation product as Kaufmann and Strübin, and, regarding the product as the diethiodide of a diquinolyl, they represented the reaction thus :

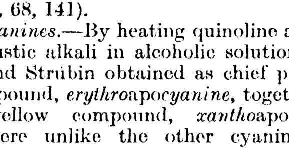
$$(C_{18}H_{13}N_2Et_2)I + I_2 = (C_{18}H_{12}N_2Et_2)I_2 + HI$$

By analogy with other cyanines they concluded that the only two diquinolyls possible were those having the 3:4- (LXIV) and 3:2-linkings (LXV) respectively, thus supporting König's formulæ. Their views were confirmed by the synthesis of 3:4′-diquinolyl and the demonstration that its diethiodide is identical with the product obtained by oxidising erythro*apo*cyanine with iodine (J.C.S. 1928, 81).



1:1′-Diethyl-3:4′-*apo*cyanine iodide.
(1-*Ethyl-3-quinoline*)(1-*ethyl-4-quinoline*)apo*cyanine iodide*.

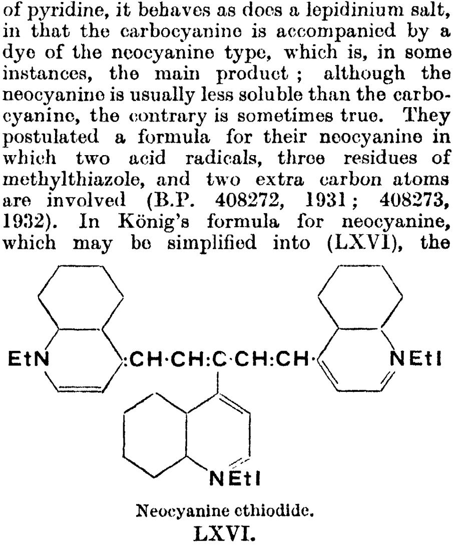
LXIV.



1:1′-Diethyl-3:2′-*apo*cyanine iodide.
(1-*Ethyl-2-quinoline*)(1-*ethyl-3-quinoline*)apo*cyanine iodide*.

LXV.

Neocyanines.—Clarke and the Eastman Kodak Co. observed that when lepidine ethiodide is treated in alcoholic solution with iodoform and alkali, there is formed, in addition to the 4:4′-carbocyanine (VIII), a less soluble dye giving a green solution (U.S.P. 1804674, 1931). This compound, *neocyanine* (or "*allocyanine*"), sensitised further into the infra-red than any dye then known (Dundon, Schoen and Briggs, J. Opt. Soc. Amer. 1926, **12**, 397; Babcock, Nature, 1928, **121**, 830). Hamer found that neocyanines also accompany (VIII) when lepidine quaternary salts are heated with ethyl orthoformate in the presence of pyridine ; by varying the conditions, the formation of one dye at the expense of the other could be favoured, and a 40% yield of neocyanine was thus obtained. It was shown analytically that the molecule contains two iodine atoms, three lepidine residues, and either one or two extra carbon atoms ; on the basis of one extra carbon atom, a formula was postulated (J.C.S. 1927, 2796; 1928, 1472). Ogata described similar dyes in which the three lepidine nuclei are replaced by quinaldine or α-picoline nuclei, and studied the effect of various reagents upon neocyanine formation (Proc. Imp. Acad. Tokyo, 1932, **8**, 503 ; Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 491 ; Ogata and Tamura, *ibid.* 475). Of these reagents, succinic acid proved interesting, and he obtained a neocyanine, in 1% yield, by heating 2-methylbenzthiazole ethiodide with succinic acid and ethyl orthoformate, and also prepared a neocyanine from 1:2-dimethylbenziminazole methiodide (*ibid.* 1934, **13**, 497). Meanwhile Brooker and Kodak Ltd. had observed that when a 2-methylthiazolium salt is heated with ethyl orthoformate, in the presence of pyridine, it behaves as does a lepidinium salt, in that the carbocyanine is accompanied by a dye of the neocyanine type, which is, in some instances, the main product ; although the neocyanine is usually less soluble than the carbocyanine, the contrary is sometimes true. They postulated a formula for their neocyanine in which two acid radicals, three residues of methylthiazole, and two extra carbon atoms are involved (B.P. 408272, 1931; 408273, 1932). In König's formula for neocyanine, which may be simplified into (LXVI), the

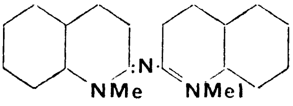


Neocyanine ethiodide.

LXVI.

number of extra carbon atoms is two; he regarded it as a substituted dicarbocyanine (Z. wiss. Phot. 1935, **34**, 15). From the absorption maxima of 4:4′-carbocyanine, 4:4′-dicarbocyanine, and neocyanine, Hamer is of opinion that the last may be regarded more correctly as a substituted carbocyanine (Chem. and Ind. 1935, **13**, 640).

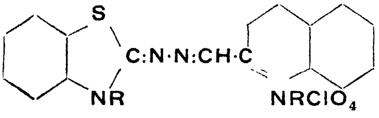
Azacyanines.—Starting from 2-aminoquinoline and 2-chloroquinoline, Hamer synthesised the 2:2′-*azacyanine* (LXVII) (then called "2:2′-*azocyanine*"), in which the linking between the two quinoline nuclei is not by :**CH**· but by :**N**·.



1:1′-Dimethyl-2:2′-azacyanine iodide.
Bis-(1-methyl-2-quinoline)azamethincyanine iodide.

LXVII.

It differed from the cyanines in that it was not decolorised by acids (J.C.S. 1924, **125**, 1348). Fuchs and Grauaug synthesised carbocyanine analogues, in which the chain :**CH**·**CH**:**CH**· is replaced by :**N**·**N**:**CH**·, by condensing a heterocyclic aldehyde (*e.g.* quinoline-2-aldehyde methoperchlorate) with the hydrazone of a heterocyclic ketone (*e.g.* 3-ethyl-2-benzthiazolone hydrazone). They prepared two dyes containing one benzthiazole and one quinoline nucleus (LXVIII), one with two benzthiazole nuclei, and one with a pyridine and a benzthiazole nucleus.

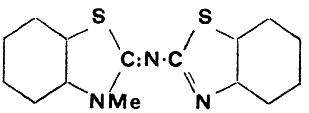


3:1′-Dialkyl-8:9-diazathia-2′-carbocyanine perchlorate.
(1-Alkyl-2-quinoline)(3-alkyl-2-benzthiazole)βγ-bisazatrimethincyanine perchlorate.

LXVIII.

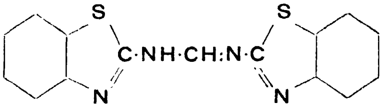
They noted that the colours of these dyes in solution vary from yellow to deep red, and they all act as photographic desensitisers (Ber. 1928, **61**, [B], 57).

Kendall, by condensing a quaternary heterocyclic ammonium salt, containing an NH_2 group in the *α*- or *γ*-position, with a similar salt, containing a reactive alkylthiol group or iodine atom, prepared various 2:4′-, 4:4′-, *oxa-*, *thia-*, *thia-2′-*, and *thia-4′-azacyanines.* When instead of a quaternary salt containing an NH_2 group, the corresponding base (*e.g.* 2-aminobenzthiazole) was subjected to such a condensation (*e.g.* with a 2-methylthiolbenzthiazole quaternary salt), a base, *e.g.* (LXIX), was obtained, of which the thia-azacyanine is the quaternary salt. By condensing a heterocyclic nitrogenous base, containing an *α*-NH_2 group as substituent, with ethyl orthoformate, Kendall obtained substituted formamidines, *e.g.* 2-aminobenzthiazole gave (LXX), which could be converted into the *diazathiacarbocyanine* (LXXI). Treatment of a 2-aminobenzthiazolium salt with ethyl orthoacetate and pyridine gave the 9-methyl derivative of (LXXI). Kendall noted that (LXVII), (LXVIII), and their analogues, and also bases such as (LXIX) and (LXX), act as sensitisers to gelatino-chloride photographic emulsions (B.P. 447038; 447109, 1934; 456419, 1935). He has postulated the theory that a substituted amino-group has the power of increasing the sensitising action of a cyanine dye when introduced in such a position that the carbon chain between it and one of the original nitrogen atoms is odd as opposed to even; similarly the sensitising properties of (LXXI), as contrasted with the desensitising properties of (LXVIII), are attributed to replacement by an odd-numbered of an even-numbered carbon chain (Proc. Ninth Internat. Congr. Phot. 1935, 227).



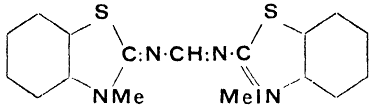
3′-Methyl-2-benzthiazolylideneaminobenzthiazole.

LXIX.



2:2′-Dibenzthiazolylformamidine.

LXX.



3:3′-Dimethyl-8:10-diazathiacarbocyanine iodide.
Bis-(3-methyl-2-benzthiazole)αγ-diazatrimethincyanine iodide.

LXXI.

Definition of a Cyanine.—A cyanine is characterised by possessing two heterocyclic nuclei containing nitrogen; one of these nitrogen atoms is tertiary and the other quaternary and they are united by a chain of conjugated double bonds, so that the number of carbon atoms in the chain is necessarily uneven; one or more :**CH**· groups in the chain may be replaced by one or more nitrogen atoms.

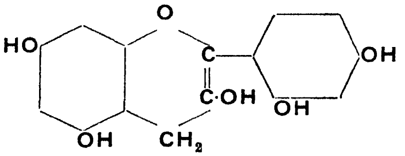
Compounds related to the Cyanines.—The above definition excludes certain types of compounds, which are sometimes described together with cyanines. Such are the following: (*a*) compounds in which both nitrogen atoms are quaternary and the chain consists of an even number of carbon atoms, (*b*) styryl compounds, to which type the sensitiser *Pinaflavol* belongs and to certain members of which type König (Z. wiss. Phot. 1935, **34**, 15) assigned the name "*semicyanines*," (*c*) the related anils, which are usually desensitisers, and (*d*) dyes prepared by condensing certain cyanine intermediates with compounds containing a reactive cyclic or noncyclic methylene group.

Nomenclature of the Cyanines.—According to the historical treatment adopted in the present article, each point of nomenclature has been dealt with as it arose, so that the system which has grown up in the British and American literature has been made clear. As it requires acquaintance with such a large number of group names, it is, however, far from satisfactory; the cyanines are now revealed as comprising a far greater number of different types than was originally contemplated, and the nomenclature has also been complicated by the fact that some of the simplest members were not amongst the first to be prepared. König pointed out the inconveniences attaching to the use of these group names, and proposed a systematic nomenclature (Ber. 1922, **55**, [B], 3293), which has, however, proved cumbersome in actual use. The system denoted in the 1936 edition of " Beilsteins Handbuch der organischen Chemie " (which deals with the literature up to 1910) has the great advantage that, once a few simple principles have been laid down, each and every cyanine can be named systematically. Such principles are as follows: (1) the above definition of a cyanine (which is narrower than that of Beilstein) is taken; (2) each ring is denoted by its usual description and numbering (following Richter's " Lexikon " and the "Journal of the Chemical Society"), and the positions of linking are indicated; (3) the number of methenyl groups linking the nuclei is denoted by *apo* (for none), methin, trimethin, pentamethin, etc.; (4) the presence of :**N**· replacing :**CH**· in the chain is denoted by the term *aza*, which is already in use in international nomenclature for :**N**· replacing :**CH** in a ring. Below the graphic formula of each cyanine in the present article has been given the name at present accepted, whilst below that, printed in italics, has been added the systematic name as arrived at from the principles formulated above.

F. M. H.

CYANOGEN *v.* CYANIDES (this vol., p. 503).

CYANOMACLURIN, $C_{15}H_{12}O_6$. A colourless crystalline compound found in Jak-wood; it is fairly readily soluble in water and gives a colourless precipitate with basic lead acetate and a violet colour with ferric chloride. When fused with alkali it gives β-resorcylic acid and phloroglucinol. The *penta-acetyl* derivative, $C_{15}H_7O_6Ac_5$, has m.p. 136–138°, the *penta-benzoyl* derivative, m.p. 171–172°. Cyanomaclurin is probably a reduction product of morin (Perkin, J.C.S. 1905, **87**, 715).



CYANOPHORIC GLYCOSIDES. A considerable number of glycosides have been isolated from plants which yield hydrogen cyanide when hydrolysed, whilst the formation of hydrogen cyanide by a plant is attributed to the presence of a glycoside. The most interesting of these is amygdalin (*q.v.*), which contains the sugar gentiobiose, as does also lotusin from *Lotus arabicus*. Vicianin, from the seeds of the wild vetch, contains the disaccharide vicianose. Cyanophoric glucosides are prunasin, prulaurasin, sambunigrin, dhurrin, gynocardin, linamarin, hiptagin.

A list of plants containing hydrogen cyanide compiled by Greshoff (Rep. Brit. Assoc. 1906, 138) and another by Rosenthaler (Chem. Zentr. 1919, iii, 274; 1930, ii, 932) enumerate 360 varieties in 148 species and 41 families. In general the presence of hydrogen cyanide in plants appears to be incompatible with that of alkaloids and terpenes. The amount of cyanophoric glycoside varies according to the conditions. Linseed, which contains linamarin, produces considerably less hydrogen cyanide when grown in this country than in the Orient, where it is grown under conditions of drought and high temperature. The cyanophoric glycosides are hydrolysed by acids and by the specific enzymes which accompany them in the plants, most of them are attacked by emulsin.

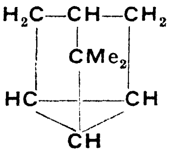
E. F. A.

CYANURIC ACID *v.* CYANIDES (this vol., p. 506).

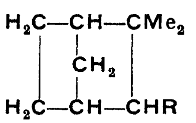
CYCLAMIN, $C_{63}H_{110}O_{32}$, m.p. 251°, $[\alpha]_D$ −22°, the saponin glycoside present in cyclamen tubers (*Cyclamen europaeum*). According to Dafert (Ber. der Pharm. Ges. 1926, *264*, 409; 1930, *268*, 289), it is hydrolysed to the aglucone, *cyclamiretin*, $C_{35}H_{56}O_5$, glucose (3 mols.) and *l*-arabinose (2 mols.).

E. F. A.

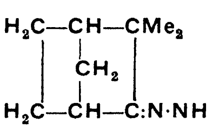
*apo*CYCLENE.



*apo*Cyclene, C_9H_{14}, m.p. 42·5–43°, b.p. 138–139°/764 mm., d_4^{40} 0·871, n_D^{40} 1·43144, is formed when camphenilyl chloride (I) is heated with diethylaniline or when camphenilol (II) is digested with potassium hydrogen sulphate at 180–190° (Komppa and Roschier, Annalen, 1922, **429**, 187; Gratton and Simonsen, J.C.S. 1935, 1621; Komppa and Nyman, Ber. 1936, **69**, [B], 338). Since it is stable to potassium permanganate it can be readily purified. According to Nametkin and Alexandrov (Annalen, 1928, **467**, 191), it can be conveniently prepared by heating camphenilone hydrazone (III) with mercuric oxide and alkali.



I. R=Cl; II. R=OH.



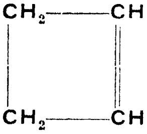
III.

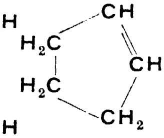
J. L. S.

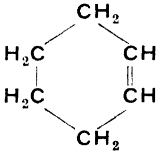
CYCLENES (CYCLIC OLEFINS).

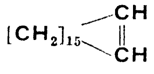
These substances do not for the most part occur naturally, although the monocyclic terpenes must be regarded as members of the group. They can, however, readily be derived from various simple derivatives of the saturated cyclic hydrocarbons (cyclanes). Mono-, di-, tri-, and tetra-olefinic members of the group are known; also different series of cyclenes are to be distinguished according to the number of carbon atoms forming the ring.

Mono-olefins.—The number of known mono-olefinic cyclenes is very large, and the various series represented by these compounds range from that in which the ring contains four carbon atoms (*cyclo*butenes) to that in which it contains seventeen carbon atoms (*cyclo*heptadecenes).


*cyclo*Butene.


*cyclo*Pentene.


*cyclo*Hexene.


*cyclo*Heptadecene.

The members of the different series are usually derived from cyclic alcohols, which in turn are derived by reduction of the corresponding cyclic ketones. The alcohols are dehydrated directly by warming them or refluxing them with small or larger amounts of suitable dehydration-catalysts (hydrobromic acid, iodine, zinc chloride, sulphuric acid, etc.) or by passage of their vapours over suitable contact catalysts (alumina, kaolin, etc.) heated to appropriate temperatures; alternatively, they are converted into the corresponding chlorides or bromides by treatment with halides of hydrogen, phosphorus or sulphur, and thence into the cyclic olefins by the action of boiling alcoholic caustic alkali, boiling quinoline or other basic reagent, or less commonly by the passage of their vapours over suitable heated dehydrohalogenation catalysts. In the *cyclo*hexene series, however, the requisite alcohols can frequently be derived in quantity by catalytic hydrogenation of the corresponding phenols (Sabatier-Senderens process), and hence *cyclo*hexene and its simpler alkyl derivatives may be prepared relatively cheaply on a commercial scale. In the case of certain dialkyl-*cyclo*hexenes (menthenes) the mono-olefinic hydrocarbons may be obtained by the partial hydrogenation of di-olefinic terpenes (menthadienes).

The mono-olefinic cyclenes are volatile liquids of petroleum-like odour and in their physical and chemical properties closely resemble the open-chain olefins. Certain physical properties

Mono-olefinic Cyclenes.

	B.p. (°C.).	*d*	n_D
*cyclo*Butene	1·5–2	$0{\cdot}733_4^0$	—
,, Pentene	44·1–44·6	$0{\cdot}7743_4^{18}$	$1{\cdot}4218^{18}$
,, Hexene	83–83·5	$0{\cdot}8102_4^{20}$	$1{\cdot}4451^{22{\cdot}1}$
,, Heptene	113–115	$0{\cdot}8228_4^{20}$	$1{\cdot}4552^{20}$
,, Octene	145	$0{\cdot}855_4^{20}$	$1{\cdot}474^{20}$
,, Pentadecene	m.p. 36–37	—	—
,, Heptadecene	m.p. 47	—	—
1-Methyl-Δ^1-*cyclo*pentene	72	$0{\cdot}7758_0^{20}$	—
1-Methyl-Δ^2- ,, ...	69	$0{\cdot}7663_4^{18}$	$1{\cdot}4222^{18}$
1:1-Dimethyl-Δ^2- ,, ...	76–78·5	$0{\cdot}7580_0^{20}$	$1{\cdot}4190^{20}$
1:2- ,, -Δ^1- ,, ...	103–103·5	$0{\cdot}7923_0^{20}$	$1{\cdot}447^{13{\cdot}5}$
1-Methyl-Δ^1-*cyclo*hexene	108	$0{\cdot}8099_0^{20}$	$1{\cdot}4496^{20}$
1- ,, -Δ^2- ,, ...	104–106	—	—
1- ,, -Δ^3- ,, ...	103	$0{\cdot}7986_0^{20}$	$1{\cdot}443^{16}$
1:2-Dimethyl-Δ^3-*cyclo*hexene	135·5–136·5	$0{\cdot}8226_4^{20}$	$1{\cdot}4580^{21{\cdot}5}$
1:4- ,, -Δ^1- ,, ...	124–126	$0{\cdot}7985_4^{22{\cdot}4}$	$1{\cdot}444^{22}$
1:1- ,, -Δ^3- ,, ...	119·5–121·2	$0{\cdot}8056_4^{16{\cdot}2}$	$1{\cdot}445^{16{\cdot}2}$
1:3- ,, -Δ^3- ,, ...	124–126	$0{\cdot}7998^{22{\cdot}6}$	$1{\cdot}4466^{21}$
1:3- ,, -Δ^4- ,, ...	126–127	$0{\cdot}8074_4^{18{\cdot}4}$	$1{\cdot}4508^{17}$

of the more important cyclenes are given in the table (p. 532). The most important of the simple cyclenes are *cyclo*pentene and *cyclo*hexene, which are respectively the parent compounds of a large array of alkyl- and polyalkyl-*cyclo*pentenes and -*cyclo*hexenes. The alkyl- and polyalkyl-derivatives of both series are almost invariably obtained from the corresponding alcohols or their halogen esters by the methods mentioned above. Allied to the cyclenes and resembling them in methods of formation and in chemical behaviour are the alkylidene-cyclanes of general formula, $(CH_2)_n{>}C{=}CRR'$.

cyclo*Propene* is reported to be formed together with other products by heating barium pyromucate, and *cyclo*butene by the distillation of trimethyl-*cyclo*butyl-ammonium iodide, but the identity of both products appears to be somewhat uncertain.

cyclo*Hexene* is a typical cyclene and is prepared on a large scale by dehydration of *cyclo*hexanol. When the latter (400 g.) is heated with concentrated sulphuric acid (12 c.c.) at 130–140°, and finally at 150°, *cyclo*hexene distils (Organic Syntheses, V, 33). The crude hydrocarbon is washed successively with alkali and with water, and is then dried and distilled (yield, 78–87%). *cyclo*Hexene reacts with chlorine, bromine, hypochlorous acid, and hydrogen (in presence of Pt or Pd) to give the corresponding chloride, bromide, chlorohydrin, and cyclane respectively, and it is oxidised by alkaline permanganate to adipic acid. On long treatment with oxygen it gives a 0·75% yield of the peroxide $C_6H_{10}O_2$, together with a syrup which is probably the dimeric peroxide (Stephens, J. Amer. Chem. Soc. 1928, **50**, 568), a much larger yield (20%) of practically pure peroxide is formed when it is irradiated in presence of oxygen (Hock and Schrader, Naturwiss. 1936, **24**, 159). This peroxide gives, (*a*) with 2*N*-sulphuric acid, *cyclo*hexanediol, m.p. 104° (50% yield), and *cyclo*pentene aldehyde (10–20% yield), and (*b*) with concentrated caustic soda, Δ^1-*cyclo*hexen-3-ol, which also is produced by reduction of the peroxide with sodium sulphite (Hock and Schrader, *l.c.*). With a 7% or a 20% ethereal solution of peracetic acid *cyclo*hexene yields *cyclo*hexene oxide, $C_6H_{10}O$, which is hydrated to the *trans* glycol, m.p. 103°, by sulphuric acid (Arbusov and Michailov, J. pr. Chem. 1930, [ii], **127**, 92); with lead tetracetate it yields 1:2-diacetoxy*cyclo*hexane, 3-acetoxy-Δ^1-*cyclo*hexene, as well as 3:3- and 3:6-diacetoxy-Δ^1-*cyclo*hexene (Criegee, Annalen, 1930, **481**, 263); with liquid sulphur dioxide in presence of a catalyst (H_2O_2) it yields a polymeric sulphone (Frederick, Cogan and Marvel (J. Amer. Chem. Soc. 1934, **56**, 1815). When its vapour, mixed with carbon dioxide, is passed over finely divided nickel at 180° it undergoes disproportionation to yield a mixture of benzene and *cyclo*hexane:

$$3C_6H_{10} \rightarrow C_6H_6 + 2C_6H_{12}$$

(Böeseken and Sillevis, Proc. K. Akad. Wetensch. Amsterdam, 1913, **16**, 499), and when it is treated with aromatic hydrocarbons in presence of anhydrous aluminium chloride, addition of the former occurs at the unsaturated centre of the cyclene (Bodroux, Compt. rend. 1928, **186**, 1005):

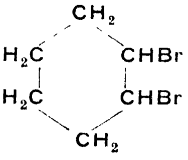
$$C_6H_{10}+CH_3{\cdot}C_6H_5 \rightarrow C_6H_{11}{\cdot}C_6H_4{\cdot}CH_3$$

$$C_6H_{10}+p\text{-}C_6H_4(CH_3)_2 \rightarrow C_6H_{11}{\cdot}C_6H_3(CH_3)_2$$

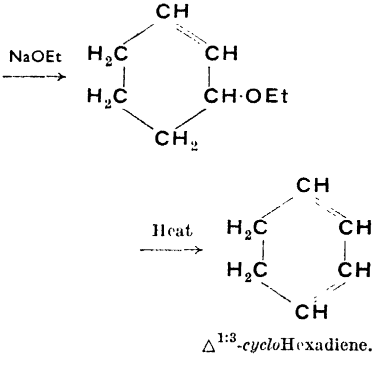
$$C_6H_{10}+1{:}3{:}5\text{-}C_6H_3(CH_3)_3 \rightarrow C_6H_{11}{\cdot}C_6H_2(CH_3)_3$$

Polymerisation of *cyclo*hexene to the dimeric stage (*cyclo*hexyl-*cyclo*hexene) can be effected with phosphoric oxide (Truffault, Compt. rend. 1935, **200**, 406), and to di-, tri-, tetra- and poly- meric stages with boron trifluoride (Hofmann, Chem.-Ztg. 1933, **57**, 5).

Di- and poly-olefins.—The most important of these are *cyclo*pentadiene, which occurs in the forerun of benzene from coal tar, and the monocyclic terpenes, various of which are contained in the essential oils of a number of plants. All other members of the group, whether containing five-carbon, six-carbon, or higher rings, are obtained by synthetic means. With the exception of *cyclo*pentadiene and the naturally-occurring terpenes (menthadienes), they are almost invariably prepared by the removal of hydrogen halide from dihalogeno-cyclanes, dihalogeno-cyclenes, or cyclic dihalogeno-dienes, either directly by the action of alkalis, *e.g.*:

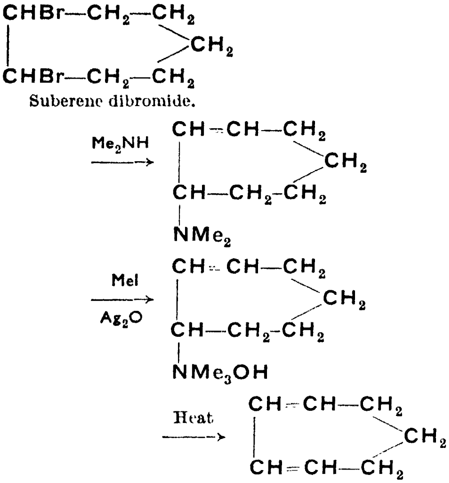


*cyclo*Hexene dibromide.



$\Delta^{1:3}$-*cyclo*Hexadiene.

or more usually by the exhaustive methylation method of Hofmann. According to the latter method the halogeno-compound is treated with an organic base and the resulting amino-compound exhaustively methylated in order to produce a quaternary ammonium salt; this salt, or more usually the corresponding quaternary ammonium hydroxide obtained from it by the action of silver oxide or caustic alkali, is distilled, whereon the basic radical is eliminated, and the unsaturated hydrocarbon formed, *e.g.*:

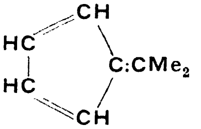


Suberene dibromide.

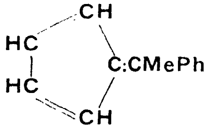
$\Delta^{1.6}$-*cyclo*Heptadiene.

It is to be remembered that elimination reactions occurring in a grouping $>CH-CHX-CH<$ may in general take two directions, yielding $>C=CH-CH<$ and $>CH-CH=C<$, so that mixtures of isomeric dienes and polyenes are frequently obtained by the above-named preparative methods. Such mixtures are usually inseparable by ordinary fractionation methods, but in these mixtures the conjugated forms appear usually to predominate over unconjugated forms. The physical properties of the more important cyclic dienes, cyclic trienes, and fulvenes are given in the table below.

cyclo*Pentadiene* may be conveniently prepared from benzene forerun which has been aged by standing for four weeks or longer after distillation. The *cyclo*pentadiene originally contained in the forerun has then largely become converted into dimeric *cyclo*pentadiene, which can readily be separated from other materials by fractionation (Perkins and Cruz, J. Amer. Chem. Soc. 1927, **49**, 517). The dimeride, containing two isomeric di-*cyclo*pentadienes, is obtained as a low-melting crystalline mass, b.p. 56°/13 mm. (Wieland and Bergel, Annalen, 1925, **446**, 19; Farmer and Scott, J.C.S. 1929, 177), which progressively reverts on slow refluxing under a short column into monomeric *cyclo*pentadiene. The latter again polymerises on standing and even after a few hours contains a measurable quantity of dimeride, with smaller quantities of higher polymerides. For the structure and stereochemistry of dimeric and trimeric *cyclo*pentadiene, *see* Ann. Reports, 1932, **29**, 113; 1936, **33**, 238. *cyclo*-Pentadiene is especially interesting in that it contains a methylene group, which, owing to its position between doubly-bound carbon atoms, is highly reactive. The hydrogen atoms of this methylene group are replaceable by alkali metals, and also react readily with the oxygen of ketones giving rise to coloured hydrocarbon condensation products of the type known as *fulvenes*, which, like *cyclo*pentadiene, are prone to undergo polymerisation.



Dimethylfulvene.



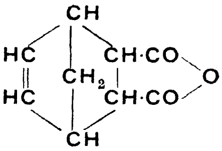
Methylphenylfulvene.

*cyclo*Pentadiene is a conjugated compound and possesses similar additive properties to the conjugated open-chain dienes. It yields two dibromides, (i) m.p. 45–46°, and (ii) an oil (Farmer and Scott, *l.c.*), and unites spontaneously and quantitatively with maleic anhydride (Diels and Alder, Annalen, 1928, **460**, 98; Alder and Stein, *ibid.* 1932, **496**, 197; Ann. Reports, 1930, **27**, 88) to give a crystalline derivative (I), which is suitable for characterisation of the hydrocarbon, and with quinone (1 mol. or 2 mols. to 1 mol. of quinone) to give

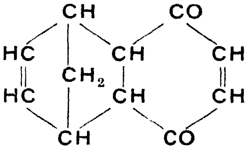
CONJUGATED CYCLIC DIENES AND POLYENES.

	B.p. (°C.)	d	n_D
*cyclo*Pentadiene	40·2–41·6	$0{\cdot}8228^{0}_{4}$	$1{\cdot}4463^{16{\cdot}2}$
„ Hexadiene	78·3–78·8	$0{\cdot}8404^{20}_{4}$	$1{\cdot}4756^{20}$
„ Heptatriene	116	$0{\cdot}8876^{18{\cdot}5}_{4}$	$1{\cdot}5213^{18{\cdot}5}_{a}$
„ Octatetraene	36·2–36·4 (14 mm.)	$0{\cdot}925^{20}_{4}$	$1{\cdot}5394^{20}$
Dimethylfulvene	49–50 (11 mm.)	$0{\cdot}881^{20}_{4}$	$1{\cdot}5474^{20}$
Ethylfulvene	74 (26 mm.)	—	—
Methylphenylfulvene	130·5 (10·5 mm.)	—	—
Diphenylfulvene	m.p. 82	—	—

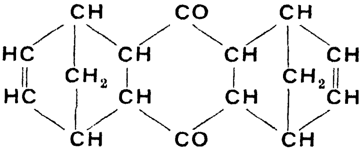
derivatives (II) and (III) which are convertible by successive elimination of the endomethylene bridges and dehydrogenation into naphthaquinone and anthraquinone respectively.



I.



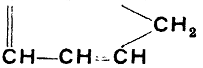
II.



III.

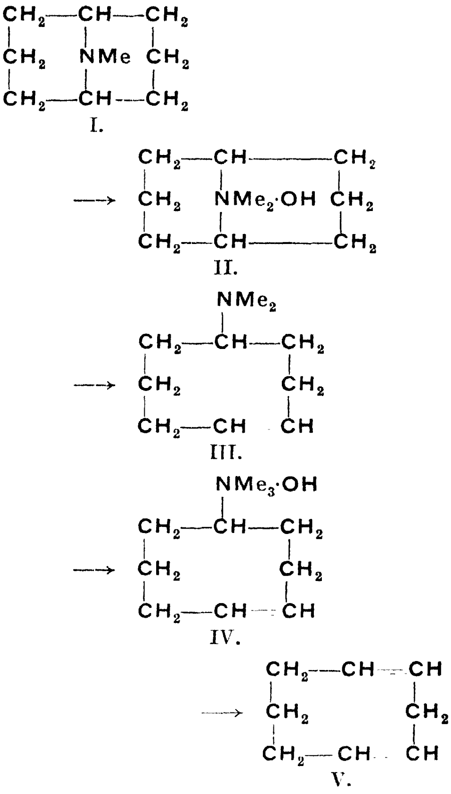
cyclo*Hexadiene* is known in conjugated ($\Delta^{1:3}$) and unconjugated ($\Delta^{1:4}$) forms, which are frequently formed together by dehydrohalogenation of various dibromo*cyclo*hexanes or dehydration of dihydroxy-*cyclo*hexanes. Pure $\Delta^{1:3}$-*cyclo*hexadiene may, however, be obtained by the action of sodium ethoxide on *cyclo*hexene dibromide (Hofmann and Damm, "mitt. schles. Kohlenforsch. Kaiser-Wilhelm-Ges." 1925, 2, 97). This substance resembles closely the open-chain conjugated diolefins: it differs from *cyclo*pentadiene in that it contains no reactive methylene group and polymerises only on prolonged heating. For the structure of dimeric *cyclo*hexadiene, *see* Alder and Stein, *l.c.*). $\Delta^{1:3}$-*cyclo*Hexadiene combines spontaneously with maleic anhydride and with quinone to give crystalline addition products analogous to those formed from *cyclo*pentadiene.

$\Delta^{1:3:6}$-cyclo*Heptatriene* (*Tropilidene*)



is a colourless liquid which readily resinifies in air. It has been obtained from *cyclo*heptene dibromide by the Hofmann method (*see above*), *cyclo*heptadiene being obtained at an intermediate stage.

cyclo*Octatetraene* has also been prepared by the Hofmann method from *N*-methylgranatanine (I), the first-formed *cyclo*octadiene (V) being converted successively into *cyclo*octatriene and *cyclo*octatetraene.



*cyclo*Octatetraene is of interest in that despite the fact that its molecule displays unbroken cyclic conjugation, it has no aromatic characteristics; moreover, it resembles in its additive properties and ease of degradation the open-chain conjugated dienes. Like benzene, its molecular refraction is normal, exhibiting no exaltation.

E. H. F.

CYCLOFORM. Trade name for the *iso*-butyl ester of *p*-aminobenzoic acid, m.p. 65°. Local anæsthetic.

CYCLONITE (*cyclo*trimethylenetrinitramine), $(CH_2{\cdot}N{\cdot}NO_2)_3$, also known as "Hexogen" and "T.4," is an explosive which in recent years has been the subject of considerable attention from the military authorities of several countries in the course of the search for more powerful fillings for bombs and other munitions. The compound was first described under the name "Hexogen" in 1899 by G. F. Henning (G.P. 104280), who prepared it by nitrating hexamethylenetetramine, the latter being derived from formaldehyde by condensation with ammonia. The material received little notice, however, until the commercial synthesis of methyl alcohol, leading to cheap supplies of formaldehyde, rendered its production on an industrial scale an economic proposition.

Manufacture.—According to E. von Herz (U.S.P. 1402693), cyclonite may be prepared on a small scale by adding 70 g. of well dried hexamethylenetetramine in small quantities to 500 g. of nitric acid (sp.gr. 1·52) with continuous stirring, the temperature being kept between 20° and 30°C. After the addition of the hexamethylenetetramine is completed, the mixture is heated slowly to 55°C., at which temperature it is maintained for 5 minutes. The mixture is then cooled to the original temperature and diluted with four times its bulk of water. The precipitated cyclonite is separated, washed first with cold water, then with hot dilute soda solution, finally with water again, and then dried. The crude material may be recrystallised from acetone.

This direct nitration of hexamethylenetetramine has been extensively studied by Hale (J. Amer. Chem. Soc. 1925, **47**, 2754), who obtained a maximum yield of 75%, using nitric acid of 100% strength and working at a temperature of −20°C.

The industrial production of cyclonite has been developed by the Nobel Dynamite Company of Avigliana (Italy) under the name of "T.4." Details of a process suitable for commercial use are given in B.P. 388615, 1932.

According to this method, hexamethylenetetramine (H/M/T) is prepared by bubbling ammonia through a saturated solution of formaldehyde, with suitable cooling. The product is acidified with nitric acid, thus precipitating the dinitrate of H/M/T, which is filtered off and dried. One part of this salt is then dissolved in 7 parts by weight of very concentrated nitric acid (the actual strength is not stated), the temperature being kept below 15°C. for the first stage of nitration. Later, the temperature is allowed to rise to 30°C., at which it is maintained for about 1 hour. The mixture is then cooled to 0°C., thus precipitating about 60% of the cyclonite, after the separation of which the liquor is distilled at a pressure of a few centimetres of mercury and at a temperature not exceeding 40°C. The nitric acid thus recovered is utilised again in the cycle of operations. The cooling and distillation operations are repeated, thus recovering further amounts of cyclonite and nitric acid. Finally, the liquor is diluted with water, thereby precipitating the remainder of the cyclonite. The dilute acid filtrate is used again for the production of H/M/T dinitrate. The filtrate and washings from the latter contain formaldehyde as a secondary reaction product. This is recovered by neutralising the acidity with chalk (or otherwise) and then concentrating and vacuum distilling the liquor. By this procedure the consumption of formaldehyde is reduced to 50% and that of nitric acid to 25% of the amounts formerly used, little more than the theoretical proportions being required.

Physical and Chemical Properties.—Crude cyclonite consists of a fine white crystalline powder, which, according to Avogadro (Mém. de l'Artillerie Française, 1931, **10**, 875) melts at 200° to 202°C., with decomposition. The crystals are of the rhombic type, their crystallographic constants being described by Terpstra (Z. Krist. 1926, **64**, 150). Large, colourless crystals may be obtained by slow crystallisation from acetone. The melting-point of the recrystallised material is given as 203·5 by Desvergnes (Chim. et Ind. 1932, **28**, 1038). Cyclonite is odourless, tasteless, non-hygroscopic, non-toxic, and unaffected by the action of light or adverse climatic conditions. Being colourless, it has no staining effect on the skin of the workers, nor does it produce any of the usual irritant effects common to most other nitro-explosives. It is stated that even after breathing appreciable quantities of the material in the form of dust no ill effects were observed.

Cyclonite is practically insoluble in cold water (0·007% at 20°C.; 0·15% at 100°C.), and very sparingly soluble in the common organic solvents, with the exception of acetone, 100 parts of which dissolve 5 parts of cyclonite at 20° and 10 parts at the boiling temperature (57·5°C.). The material is also soluble in strong nitric acid, acetic acid, and hot formic acid. From these solutions it is precipitated unchanged on dilution with water. The bulk density of the powder is stated by Avogadro to vary between 0·8 and 0·9, the absolute density of the crystals being 1·83, which is higher than that of any other nitro-compound (except tetra-nitraniline) hitherto used as an explosive. Under high pressure the powder can be compressed to an apparent density of 1·69. The compound is very stable to heat, no change in weight or appearance being observed after storing for two months at 100°C., or after 48 hours at 120°C. When stabilised by boiling with water and then submitted to the Abel heat test at 80°C., cyclonite produced no coloration on the starch iodide test paper up to 60 hours. On being heated slowly to 202°C., the material melts and begins to decompose, with evolution of gas. If the temperature is raised still further, the decomposition proceeds rapidly to completion. If heated suddenly to 280°C., the material explodes violently. When ignited with a flame, however, it burns briskly without exploding, the flame having a reddish tinge.

Cyclonite is normally regarded as a neutral compound, although according to Henning its solution in acetone has a weakly acid reaction. The material is unaffected by dilute alkalis, differing markedly from T.N.T. and similar nitro-explosives in this respect. It is equally resistant to dilute acids and to concentrated hydrochloric acid. It is decomposed, however, by concentrated sulphuric acid with evolution of gas, and is similarly attacked when heated with concentrated alkalis. According to Desvergnes it is not possible to estimate cyclonite by the nitrometer method owing to the fact that only about five-sixths of the total nitrogen is liberated as NO. Rathsburg, however, found that the material was reduced quantitatively to $C_3H_6N_6$ by titanium trichloride (Ber. 1921, **54**, [B], 3183).

Explosive Properties.—According to Kast, cyclonite detonates in accordance with the following equation,

$$C_3H_6N_6O_6 = 2CO + CO_2 + 2H_2O + H_2 + 3N_2,$$

giving a heat of explosion of 1390 kg.-cal. per kg. More recent work, however, places this figure at 1,290 kg.-cal., a larger proportion of the carbon remaining as the monoxide than is indicated by the above equation (Nitrocellulose, 1935, **6**, 24). Avogadro gives the following constants for cyclonite, the corresponding figures for T.N.T. being shown in brackets by way of comparison: velocity of detonation, 8,380 m. per sec., at density 1·70 (*cf.* 6,700 m. per sec. for T.N.T. at density 1·58); gas evolved on detonation 908 litres per kg. at N.T.P. (T.N.T. 690 l. per kg.); lead block expansion (Trauzl) test 520 ml. (T.N.T. 310 ml.); compression test (Kast apparatus), 5·2 mm. (T.N.T. 3·6 mm.); figure of insensitivity (Berthe, 2 kg. wt.), 42 cm. (T.N.T. 80, picric acid 60).

Application.—The high velocity of detonation coupled with the large volume of gas liberated and the high density of the original material render cyclonite superior in blasting power and "brisance" to any other explosive hitherto used for bursting charges, not excluding blasting gelatine. In his original patent, Herz suggested that cyclonite might be employed as a bursting charge for projectiles and mines, as a blasting explosive, as a filling for detonating fuze, as an ingredient in percussion caps and detonators, and also as a secondary initiator in fuzes for projectiles. Its use as a propellant is described in G.P. 298539 and G.P. 299028, the following mixture being said to have good ballistic properties: cyclonite 45, guncotton 30, nitrobenzene 10, trinitroanisole 9·4, and tetranitroanisole 5·6%. G.P. 469721, 1927, also described a propellant consisting of cyclonite "phlegmatised" with paraffin or carnauba wax, or with nitroaromatic bodies.

The high melting-point of cyclonite precludes the possibility of pouring it in a molten condition into projectiles or mines. By mixing it, however, with a suitable proportion (from about 30% upwards) of a more easily fusible explosive such as T.N.T., a plastic mixture is obtained which can be poured or screw-filled into the ammunition concerned at a temperature below 100°C. The use of such mixtures also reduces the risk arising from the rather high sensitivity of pure cyclonite without seriously detracting from the superior explosive power of the latter material. In this connection it was observed that when a rifle bullet was fired into a bomb filled with pure cyclonite, the latter ignited but did not explode, and the flame soon went out. A stream of bullets from a machine gun, however, caused explosion of the filling (Avogadro, *l.c.*).

In spite of the difficulties indicated, the future of cyclonite as a major high explosive for military use is regarded as highly promising.

H. S.

CYCLOPARAFFINS (NAPHTHENES) IN PETROLEUM. Crude petroleum is a mixture of hydrocarbons in which paraffins, cycloparaffins, benzenoid and polynuclear hydrocarbons occur. It has been surmised that *cyclo*propane and *cyclo*butane occur in natural gas, although the evidence is not very conclusive. In the subsequent fractions prepared by the distillation of petroleum undoubtedly there is a long series of cycloparaffins, but the separation of naphthenes from paraffins is extremely difficult, even although naphthenes and paraffins can be segregated from other hydrocarbons by the use of specific solvents, as, for example, nitrobenzene and phenols.

In the motor spirit fraction *cyclo*pentane and *cyclo*hexane and their homologues are the main cycloparaffin components. There is evidence that dimethyl*cyclo*butane occurs in Californian petroleum and *cyclo*heptane in Russian oil. The latter hydrocarbon appears to be present in many natural crude oils as does also methyl*cyclo*pentane. *cyclo*Hexane occurs in Russian gasoline and has been identified in some of the American crudes. Of the other homologues dimethyl*cyclo*hexane, trimethyl*cyclo*hexane and dimethylethyl*cyclo*hexane have been obtained from a variety of crudes, *e.g.* American, Russian, Galician, Borneo and Japanese.

In the kerosene fractions the identification is very much more difficult. Nevertheless, it has been surmised that certain bicyclic hydroaromatic hydrocarbons occur. It is still more difficult to identify hydrocarbons of this type in the higher fractions, *e.g.* lubricating oils, and, in point of fact, there is very little precise information as to the chemical nature of any of the hydrocarbon components of high boiling-point.

In the cracking of petroleum cycloparaffins are produced and they conceivably are formed by the cyclisation of preformed olefins. In the case of cracked Russian kerosene, methyl*cyclo*pentane, *cyclo*hexane, dimethyl*cyclo*pentane and methyl*cyclo*hexane were identified in the products. So much as 30% of naphthenes have been obtained in an average cracked spirit. Special reference should be made to Carleton Ellis, "The Chemistry of Petroleum Derivatives," Rheinhold & Co.

A. E. D.

CYCLORANE. Potassium oleate + a higher alcohol (b.p. above 160°), used as a wetting-out agent.

CYGNINE, $C_{12}H_{22}O_3N_2$, is said to have been isolated from *Gastrolobium calycinum* (Leguminosæ of Western Australia) by Mann and Ince (Proc. Roy. Soc. 1907, **79**, B, 485). A way of preparing the amorphous alkaloid is described, and also the properties of the free base, the hydrochloride and the chloroaurate, but the report suggests further enquiry.

Schl.

CYLINDRITE. (Ger. *Kylindrit.*) A complex sulphide ore of tin, $Pb_3FeSn_4Sb_2S_{14}$, containing, according to this formula, Sn 25·85%. It forms very peculiar cylindrical rolls of thin folia, the concentric shells parallel to the axis of the cylinder readily separating under pressure. The smooth, bright surfaces of separation no doubt represent the cleavages of cylindrically curved crystals. The colour is blackish lead-grey, with a brilliant metallic lustre. The mineral marks paper, and is difficult to pulverise, in these respects resembling graphite. The ore consists of numbers of these rolls, which measure up to 3 cm. in length and 1 cm. in diameter, confusedly aggregated together, or sometimes with a sub-parallel grouping, the interspaces being filled with massive material. It has been found in some quantity in the Santa Cruz mine, at Poopó, Bolivia. The above formula, written in the form

$$3PbSnS_2+SnFeSb_2S_8,$$

brings out a relation between cylindrite and the allied Bolivian minerals, *teallite* ($PbSnS_2$) and *franckeite* ($3PbSnS_2+Pb_2FeSb_2S_8$). Analyses I and II, by G. T. Prior (Min. Mag. 1904, **14**, 21); III, by A. Frenzel (Jahrb. Min. 1893, **2**, 124); IV, E. G. J. Hartley (J.C.S. 1936, 1292); V, F. M. Brewer and E. Baker (J.C.S. 1936, 1292).

	I.	II.	III.	IV.	V.
Pb . . .	35·24	34·58	35·41	33·97	38·65
Fe . .	2·81	2·77	3·00	3·47	—
Ag . .	0·50	0·28	0·62	nil	nil
Sn . .	25·65	25·10	26·37	25·06	21·44
Sb . .	12·31	12·98	8·73	11·92	7·74
S . . .	23·83	23·88	24·50	24·39	23·75
	100·34	99·59	98·63	98·81	91·58
Sp.gr. . .	5·46	5·49	5·42	—	—

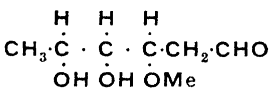
L. J. S.

CYMARIN, $C_{30}H_{44}O_9$, m.p. 130°, $[\alpha]_D$ +23°, is the simple cymarose glycoside of strophanthidin, *i.e.* $C_7H_{13}O_3{\cdot}O{\cdot}C_{23}H_{31}O_5$. It is present in Canadian hemp and various species of Apocynum. Crystalline *Kombé* strophanthin is a mixture of cymarin with the glycoside of strophanthobiose (Jacobs and Hoffmann, J. Biol. Chem. 1926, **67**, 609; **69**, 153; 1928, **79**, 531).

E. F. A.

CYMAROSE, $C_7H_{14}O_4$, m.p. 88°, is the sugar obtained from the strophanthidin glycoside cymarin, present in Canadian hemp as well as in periplocymarin from *Periploca græca*.

It was shown by Jacobs and Hoffmann (J. Biol. Chem. 1926, **67**, 609; **69**, 153; 1928, **79**, 531) to be probably a methyl ether of digitoxose, and since it gives rise to hydroxymethoxyglutaric acid on oxidation with nitric acid (Elderfield, Science, 1935, **81**, 440; J. Biol. Chem. 1935, **111**, 527), the position of the methoxy group is located as:



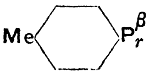
$$CH_3{\cdot}\underset{OH}{\overset{H}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{OMe}{\overset{H}{C}}{\cdot}CH_2{\cdot}CHO$$

A possible isomeride, sarmentose, has been obtained in crystalline form, m.p. 78°, $[\alpha]_D$ +12°, increasing to +15·8°, from the sarmentocymarin of *Strophanthus sarmentosus* (Jacobs and Bigelow, J. Biol. Chem. 1932, **96**, 355, 449).

E. F. A.

CYMENES (CYMOLS), $C_{10}H_{14}$. The name cymene was first given to the hydrocarbon isolated by Gerhardt and Cahours (Ann. Chim. Phys. 1841, [iii], **1**, 102, 372) from Roman oil of cumin, which is the ethereal oil of *Cuminum cyminum.* This hydrocarbon was originally called *p*-methylpropylbenzene, but Widman (Ber. 1891, **24**, 439, 970, 1632) proved it to be the *iso*propyl compound. Frequently the various benzene hydrocarbons of the formula $C_{10}H_{14}$ are grouped together under the collective name of cymenes. The following is a brief account of the more important of these hydrocarbons.

p-*Methyl*iso*propylbenzene* (p-*Cymene*),



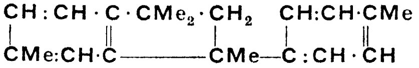
Occurrence.—*p*-Cymene occurs widely distributed in the essential oils of gymnosperms and Angiosperms, and, more especially, in those of the Umbelliferæ and Labiatæ (Semmler, "Die Aetherischen Oele," iv, 19). Considerable quantities of crude cymene, known as sulphite turpentine, collect on the surface of the liquid in the separator used in recovering sulphur dioxide in the manufacture of wood pulp. Cymene also occurs in certain petroleums.

Formation and Preparation.—Many of the terpenes $C_{10}H_{16}$ and their derivatives may be readily converted into cymene. Camphor on dehydration yields mixtures of *m*- and *p*-cymene in proportions varying with the dehydrating agent used. *p*-Cymene is produced from dipentene when the latter is shaken with concentrated sulphuric acid (Wallach and Brass, Annalen, 1884, **225**, 311) and more than 68% of *p*-cymene is formed when citral is distilled with a little iodine (Bogert and Fourman, Amer. Perfumer, 1933, **28**, 345). The most economical methods of preparing cymene from terpenes are discussed by E. Raymond (Bull. Soc. chim. 1934, [v], **1**, 1470).

Cymene has been synthesised by many of the classical methods, *e.g.* from *p*-bromocumene (*p*-bromo*iso*propylbenzene), methyl iodide, and sodium in ether (Widman, Ber. 1891, **24**, 450), or from *iso*propyl chloride, toluene, and aluminium chloride (Silver, Bull Soc. chim. 1884, [ii], **43**, 321). It may be prepared by the action of *iso*propyl sulphate on magnesium *p*-tolyl bromide (Bert, Compt. rend. 1923, **177**, 452; Bull. Soc. chim. 1925, **37**, 1252, 1397). It is produced by the alkylation of toluene with propylene or *iso*propyl alcohol using various catalysts, *e.g. see* J. Amer. Chem. Soc. 1935, **57**, 883–4, for use of propylene and phosphoric oxide; J. Gen. Chem. Russ. 1935, 5117, for use of *iso*propyl alcohol and aluminium chloride; Compt. rend. 1935, **200**, 466, for use of *iso*propyl alcohol and sulphuric acid.

Properties.—*p*-Cymene is a liquid, b.p. 177–177·5° (corr.), $d_{4}^{7\cdot9}$ 0·8670 (Perkin, J.C.S. 1896, **69**, 1195; 1900, **77**, 279), m.p. −75°.

Reactions.—For a general study of the chlorination, nitration and sulphonation of *p*-cymene, *see* T. Kuan (J. Chem. Soc. Japan, 1931, **52**, 473); *p*-cymene nitrates successively in the 2- and 6-positions (Ber. 1887, **21**, 2126; J. Amer. Chem. Soc. 1927, **49**, 494). Sulphonation gives the 2-sulphonic acid (Le Fèvre, J.C.S. 1934, 1501). Chlorination occurs successively in the 2-, 5-, 6-, and 3-positions, and the higher chlorination products are accompanied by chlorotoluenes formed by replacement of the *iso*propyl group with chlorine (Quist and Holmberg, Acta Acad. Aboensis. Math. Phys. 1932, **6**, No. 14, 3). Bromo and iodo derivatives are known. On oxidation *p*-cymene yields terephthalic acid, toluic acid, *p*-α-hydroxy*iso*propylbenzoic acid, methyl *p*-tolyl ketone, any of which can be obtained in fair yield under suitable conditions. Catalytic oxidation in the vapour phase over vanadium pentoxide, and in the liquid phase using manganese dioxide have been studied (Ind. Eng. Chem. 1931, **23**, 1129; 1932, **24**, 1184). In the former case *p*-toluic acid, and in the latter *p*-toluic acid and methyl *p*-tolyl ketone are formed. Cymene is oxidised intestinally to cumic acid. With nitrosyl sulphuric acid in the cold *p*-cymene undergoes condensation, giving 83% of a *dicymene*



(Puranen, Ann. Acad. Sci. Fennicæ, 1933, **37A**, no. 10).

Tetramethylbenzenes:

1. *Consecutive tetramethylbenzene* (*Prehnitene*), $C_6H_2(CH_3)_4$ (1:2:3:4). When sodium durenesulphonate,

$C_6H(CH_3)_4SO_3Na$(CH_3-groups 1:2:4:5)

(*v. infra*), is dissolved in concentrated sulphuric acid and allowed to stand for 12 hours, prehnitenesulphonic acid is formed. The mixture is diluted with water saturated with barium carbonate, the barium salts converted into sodium salts, and these, by treatment with phosphorus pentachloride and ammonia, transformed first into sulphonic chlorides and then into sulphonamides. Prehnitenesulphonamide is separated by means of its sparing solubility in alcohol, and is then hydrolysed by heating with concentrated hydrochloric acid to 170°, when it yields prehnitene (Jacobsen, Ber. 1886, **19**, 1213; *see also* V. Meyer and Molz, Ber. 1897, **30**, 1278). The conversion of durene and *iso*durenesulphonic acids into prehnitene by the action of strong sulphuric acid is considered in No. VI of a series of papers on the polymethylbenzenes by Smith and Cass (J. Amer. Chem. Soc. 1932, **54**, 1614).

Prehnitene may also be obtained by heating bromopseudocumene,

$C_6H_2(CH_3)_3Br$, (CH_3, Br, CH_3, CH_3, 1:2:3:4),

with methyl iodide, benzene and sodium at 150° for 12 hours. It occurs with 1:2:5:6 tetramethylbenzene among the products of dehydrogenation of certain "polyterpinoid" compounds (*i.a. see* Ruzicka *et al.*, Helv. Chim. Acta, 1934, **17**, 426; Naller, J. Amer. Chem. Soc. 1934, **56**, 1582.

Prehnitene has b.p. 204° and m.p. −4°.

(2) *Unsymmetrical tetramethylbenzene* (*iso*-Durene), $C_6H_2(CH_3)_4$, (1:2:3:5.)—*Iso*durene may be prepared by the action of dimethyl sulphate on a solution of the Grignard reagent from bromomesitylene (Organic Syntheses, XI, 66). It has b.p. 85–87°/18 mm.

Symmetrical tetramethylbenzene (*Durene*), $C_6H_2(CH_3)_4$ (1:2:4:5).—In coal tar (Ber. 1885, **18**, 3032). Preparation:—by the action of sodium on a mixture of bromopseudocumene, $C_6H_2(CH_3)_3Br$ (1:2:4:5), methyl iodide (Jannasch and Fittig, Zeitsch. Chem. 1870, 161); from toluene and methyl chloride in presence of aluminium chloride (Friedel and Crafts Ann. Chim. Phys. 1884, [vi], **1**, 461); from *o*- or *p*-xylene, methyl chloride, and aluminium chloride (Jacobsen, Ber. 1881, **14**, 2629). The durene formed by the two last methods may readily be separated from the accompanying isomeric tetramethylbenzenes on account of its much higher melting-point (Organic Syntheses, X, 32).

Durene has a camphor-like odour, m.p. 79–80°, b.p. 189–191°. On oxidation with potassium permanganate it is ultimately converted into pyromellitic acid,

$C_6H_2(CO_2H)_4$ (1:2:4:5).

CYMOLS *v.* Cymenes.

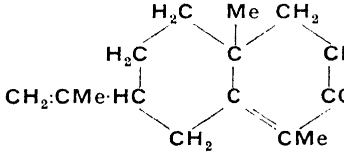
CYMOPHANE, "oriental cat's eye" *v.* Chrysoberyl.

CYNANTHRENE *v.* Antraquinone Dyestuffs.

CYNTHIAXANTHIN. This pigment, which closely resembles zeaxanthin, is associated with an ester of astacene in *Cynthia* (*Halocynthia*) *papillosa*. It separates from alcohol in needles, m.p. 188–189°, and exhibits absorption maxima at 517, 484 and 452 mμ in carbon disulphide (Lederer, Compt. rend. Soc. Biol. 1934, **117**, 1086).

I. M. H., R. F. P., and F. S. S.

α-CYPERONE.



The sesquiterpene ketone, *α-cyperone*, $C_{15}H_{22}O$, b.p. 177°/20 mm., d_{25}^{25} 0·9945, n_D^{25} 1·5283, $[\alpha]_{5461}$ +138°, $[\alpha]_{5780}$ +118·6°, forms the main constituent of the oil from the tubers of *Cyperus rotundus* (Hegde and Rao, J.S.C.I. 1935, **54**, 387T) and it has been characterised by the preparation of a number of derivatives, the more important being the *oxime*, m.p. 150·5°, *semicarbazone*, m.p. 216°, 2:4-*dinitrophenylhydrazone*, m.p. 208–209°. When digested with alkali or with oxalic acid it yields the stereoisomeric ketone, *β-cyperone*, b.p. 175–176°/16 mm., d_{25}^{25} 0·9945, n_D^{25} 1·5414, $[\alpha]_{5461}$ +239°, *oxime*, m.p. 138°, *semicarbazone*, m.p. 207°, *dinitrophenylhydrazone*, m.p. 218–219°.

The structure of α-cyperone has been determined by Bradfield, Hegde, Rao, Simonsen and Gillam (J.C.S. 1936, 667) and by Bradfield, Pritchard and Simonsen (*ibid.* 1937, 760).

The constitutions assigned to α- and β-cyperones have been confirmed by their synthesis (Adamson, McQuillin, Robinson and Simonsen, *ibid.* 1937, 1576).

L. J. S.

CYPRESS CAMPHOR *v.* Cedrol.

CYPRIAN VITRIOL. *Copper sulphate* (*v.* Copper).

CYRTOLITE, a variety of zircon.

CYSTAZOL. A urinary antiseptic containing hexamethylenetetramine and sodium benzoate. (*Allen and Hanburys, London*). B.P.C. 1934.

CYSTEINE *v.* CYSTINE.

CYSTINE. *β-disulphido-a-aminopropionic acid,*

$$HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

was first discovered by Wollaston in a urinary calculus (Phil. Trans. 1810, 223); Drechsel isolated it from the liver of horse (Arch. Anat. Physiol. 1891, 243) and porpoise (Z. Biol. 1896, **33**, 85); it was found by Külz (*ibid.* 1890, **27**, 415) among the soluble products of an artificial pancreatic digestion of fibrin; Mörner showed it was a product of the hydrolysis of several proteins, being especially abundant in keratins (Z. physiol. Chem. 1899, **28**, 595; 1901, **34**, 207). It is now recognised as a constituent of nearly all proteins. Buchtala (*ibid.* 1907, **52**, 474) obtained the following percentages of cystine from the materials mentioned: human hair, 13–14·5; human nails, 5·15; horsehair, 7·98; horse's hoofs, 3·20; ox hair, 7·27; hoofs of oxen, 5·37; pigs' bristles, 7·22; pigs' hoofs, 2·17. For the cystine content of grasses and its relation to wool crop, *see* Pollard and Chibnall (Biochem. J. 1934, **28**, 326).

For the importance of cystine in metabolism, *see* Abderhalden (Z. physiol. Chem. 1915–16, **96**, 1–147; Ber. 1916, **49**, 2449–2473), and Lewis (Physiol. Rev. 1924, **4**, 394). In view, however, of the recent discovery of a new sulphur-containing amino-acid, *methionine*, much of our knowledge of the physiological rôle of cystine is under revision (*see* articles by Lewis and du Vigneaud in Annual Rev. Biochem. 1933, 1935, and 1936).

When cystine is given with food, it is largely oxidised to sulphate and excreted as such (Rothera, J. Physiol. 1905, **32**, 175; du Vigneaud, Craft and Loring, J. Biol. Chem. 1934, **104**, 81). Baumann and Preusse (Z. physiol. Chem. 1881, **5**, 309; Ber. 1885, **18**, 258) found that when bromobenzene was administered to animals it was excreted as *bromophenylcysteine*,

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}C_6H_4Br,$$

a compound crystallising in glittering needles or plates; m.p. 180–182°, and yielding a blue crystalline *copper salt*, $(C_9H_9BrSNO_2)_2Cu$.

According to Folin (J. Biol. Chem. 1910, **8**, 9), cystine is most readily prepared from wool or hair by boiling it in a reflux apparatus for 5–6 hours with twice its weight of strong hydrochloric acid, or until it ceases to give the biuret reaction; on removing the free hydrochloric acid by the addition of solid sodium acetate, a dark heavy precipitate of cystine is obtained; this is purified by decolorising a solution in 3–5% hydrochloric acid with bone-black, and precipitating the cystine in the hot filtrate by hot concentrated sodium acetate solution There are various modifications of this method which differ mainly in the manner of the removal of the free hydrochloric acid and the final purification (Denis, J. Biol. Chem. 1911, **9**, 365; Harris, Proc. Roy. Soc. 1922–23, B, **94**, 441; Schmidt, J.C.S. 1922, **122**, i, 992; Okabe, J. Biochem. Tokyo, 1928, **8**, 441; Toennies and Bennett, J. Biol. Chem. 1936, **112**, 39).

The cystine of urinary calculus is identical with that obtained from protein hydrolysis (Rothera, J. Physiol. 1905, **32**, 175; Alsberg and Folin, Amer. J. Physiol. 1905, **14**, 54; Fischer and Suzuki, Z. physiol. Chem. 1905, **45**, 405), and was proved to be *β-disulphido-a-aminopropionic acid*) by Friedmann (Beitr. Chem. Physiol. Path. 1902, **2**, 433). This view of its constitution was confirmed by the synthesis of racemic cystine from ethyl monobenzoylserine, obtained by reducing ethyl formylhippurate, the product of the condensation of ethyl formate and ethyl hippurate. On heating ethyl monobenzoylserine with phosphorus pentasulphide and hydrolysing the product, *cysteine* is obtained, and this is readily converted into cystine by oxidation with air in an ammoniacal solution:

$$\begin{array}{l}
H{\cdot}CO_2Et + NHBz{\cdot}CH_2{\cdot}CO_2Et \\
\rightarrow CHO{\cdot}CH(NHBz){\cdot}CO_2Et \\
\rightarrow OH{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et \\
\rightarrow SH{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et \\
\rightarrow SH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \\
\rightarrow S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \\
\quad\; | \\
\quad S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H
\end{array}$$

(Erlenmeyer, Ber. 1903, **36**, 2720). Fischer and Raske (*ibid.* 1908, **41**, 893) also obtained *r*-cystine from *dl-a*-amino-*β*-chloropropionic acid hydrochloride by heating it with barium hydrosulphide at 100° in sealed tubes, and oxidising the product by atmospheric oxygen in the presence of ammonia. From the natural *l*-serine the authors obtained, by a similar process, an optically active cystine which is identical with the *l*-cystine obtained from natural sources. Removal of sulphur by ammoniacal copper solution or by zinc gives *dl*-alanine (Mauthner, Z. physiol. Chem. 1912, **78**, 30).

Cystine crystallises in thin colourless hexagonal plates; it has no melting-point, but decomposes slowly at 258–261° (Neuberg and Mayer, Z. physiol. Chem. 1905, **44**, 472). It is sparingly soluble in water, insoluble in alcohol or acetic acid, soluble in acids or alkalis. The heat of combustion at constant pressure is 4,137 g.-cal. (Emery and Benedict, Amer. J. Physiol. 1911, **28**, 301–307). The cystine molecule contains two asymmetric carbon atoms, and *lævo*-cystine, the naturally occurring variety, has $[a]_D$ −97·5°, in ammonia, −223° in hydrochloric acid solution (Gaskell, J. Physiol. 1907, **36**, 142); Toennies, Lavine, and Bennett (J. Biol. Chem. 1936, **112**, 493) have studied the specific rotation at different p_H values and found $[a]_{Hg}$ −225° at p_H 0·1; −325° between p_H 3 and 7 and −97° at p_H 11·6. *l*-Cystine is converted to the extent of 50% into *r*-cystine by heating with excess of hydrochloric acid of sp.gr. 1·124, at 165° for 12–15 hours; this decomposes at the same temperature as the active isomeride, is three times as soluble in water, and can be resolved into the active components by the action of *Aspergillus niger*, the *l*- compound being consumed.

Hollander and du Vigneaud give a method

for the resolution of inactive cystine and the isolation of *d*-cystine (J. Biol. Chem. 1931, **94**, 243).

Cystine is readily reduced to **cysteine** (*α-amino-β-thiolpropionic acid*), $HS\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ (Baumann, Z. physiol. Chem. 1882, **8**, 300; Mauthner, Z. Biol. 1901, **42**, 176; du Vigneaud, Audrieth, and Loring, J. Amer. Chem. Soc. 1930 **52**, 4,500; Gebauer-Fülnegg, *ibid.* 4610). A solution of cystine irradiated with a quartz lamp gives about 5% cysteine (Szendrö, Lampert and Wrede, Z. physiol. Chem. 1933, **222**, 16). Cysteine readily yields cystine on oxidation, the change occurring spontaneously in alkaline solution, although the rate is increased by the addition of a mixture of ferric chloride and potassium cyanide (Mathews and Walker, J. Biol. Chem. 1909, **6**, 289).

Cysteine and its derivatives are extremely active in facilitating oxidations and reductions in the tissues and it is probable that cystine derives much of its importance in the animal body from the fact that it is a source of cysteine. The most active derivative of cysteine in this respect is *glutathione, γ-glutamyl-cysteinylglycine*, which has been synthesised by Harington and Mead (Biochem. J. 1935, **29**, 1602). This tripeptide has been extensively investigated by Hopkins and co-workers who have shown its occurrence in most tissues in which it promotes oxidation and reduction processes (Biochem. J. 1921, **15**, 286; 1925, **19**, 787; J. Biol. Chem. 1922, **54**, 527; 1929, **84**, 269; Proc. Roy. Soc. 1931, B, **109**, 58; Biochem. J. 1932, **26**, 785, 817; 1935, **29**, 108).

Cysteine and cystine can be oxidised by bromine and iodine to *cysteic acid* (*α-amino-β-sulphopropionic acid*),

$$HO_3S\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

and from this, by loss of carbon dioxide, *taurine*, $NH_2\cdot CH_2\cdot CH_2\cdot SO_3H$, is obtained (Friedmann, Beitr. Chem. Physiol. Path. 1902, **2**, 433). According to von Bergmann (*ibid.* 1903, **4**, 92), the normal taurine in the bile originates from the cystine. The oxidation of cystine and cysteine to cysteic acid has been studied in some detail by Shinohara (J. Biol. Chem. 1932, **96**, 285) using iodate and by Preisler and Preisler (J. Physical Chem. 1934, **38**, 1099) using thallic sulphate. The oxidation with bromine and iodine has also been applied as a method of quantitative estimation (*v. infra*).

Cystine does not react quantitatively with nitrous acid in van Slyke's method for the estimation of amino-nitrogen (Ber. 1910, **43**, 3170). This is probably due to the -SH group being converted in part to sulphuric acid (Lough and Lewis, J. Biol. Chem. 1934, **104**, 601).

Cystine and tyrosine can be quantitatively separated by means of absolute alcohol saturated with hydrogen chloride (Plimmer, Biochem. J. 1913, **7**, 311). The separation of cystine by means of its copper salt is described by Vickery and Leavenworth (J. Biol. Chem. 1929, **83**, 523). They have also investigated the precipitation of cystine as silver salt (*ibid.* 1930, **86**, 129). When cystine in dilute sulphuric acid is treated with silver sulphate and the mixture adjusted to p_H 6, 70–85% is deposited, but the precipitate when decomposed with hydrochloric acid yields cysteine. Accompanying this reduction a small part of the cysteine is oxidised to cysteic acid. The silver compound appears to be a mercaptide. A similar behaviour of cystine with mercuric sulphate has been observed by Andrews and Wyman (*ibid.* 1930, **87**, 427) and Simonsen (*ibid.* 1931, **94**, 323).

For the estimation of cystine several methods are available. Harris uses direct isolation (Proc. Roy. Soc. 1923, B, **94**, 441) and Vickery and White precipitate cystine as cysteine cuprous mercaptide and estimate the S (J. Biol. Chem. 1933, **99**, 701). Rossouw and Wilken-Jorden (Biochem. J. 1935, **29**, 219) and Medes and Padis (*ibid.* 1936, **30**, 942, 1293) also precipitate as cuprous mercaptide but recover the cysteine and estimate by Folin's method (*see below*). Volumetric methods for the estimation of cysteine and cystine are based on their oxidation to cysteic acid by bromine and iodine. The reaction is markedly affected by temperature and hydrogen ion concentration (Okuda, A. 1926, 190; 1927, 996; 1929, 730; Lucas and King, Biochem. J. 1932, **26**, 2076; Baernstein, J. Biol. Chem. 1930, **89**, 124; Virtue and Lewis, *ibid.* 1934, **104**, 415; Lavine, *ibid.* 1935, **109**, 141). The colorimetric methods are all essentially based on colour reactions of cysteine (formed in the case of cystine by reduction with a suitable reagent) and can be adapted for the estimation of cystine, cysteine, or both. That most frequently employed is Folin's and is based upon the blue colour formed by cysteine with phosphotungstic acid. Cystine is reduced by sodium sulphite (Folin and Looney, *ibid.* 1922, **51**, 421; **54**, 171). The method has been modified in several details (Hunter and Eagles, *ibid.* 1927, **72**, 177; Folin and Marenzi, *ibid.* 1929, **83**, 89; Rimington, Biochem. J. 1930, **24**, 1114; Tompsett, *ibid.* 1931, **25**, 2014; Shinohara, J. Biol. Chem. 1935, **109**, 665; **110**, 263). Another method much used recently is Sullivan's (A. 1926, 1266; 1930, 199, 1604), which depends upon the formation of a red colour when cysteine reacts with 1:2-naphthaquinone. In the presence of sodium hyposulphite the reaction is not given by ergothionine or methionine and only by cystine in the presence of a suitable reducing agent. The method has been modified by Lugg (Biochem. J. 1933, **27**, 668, 1022) and Bushill, Lampitt, and Baker (*ibid.* 1934, **28**, 1293). The methods of Folin—Looney, Folin,—Marenzi, Sullivan, and Okuda are compared by Sullivan and Hess (A. 1930, 1604).

On heating a solution of cysteine with dimethyl-*p*-phenylenediamine and ferric chloride a blue colour is obtained which is claimed to be specific for cysteine and distinct from the methylene blue reaction for sulphides (Fleming, Biochem. J. 1930, **24**, 965).

Derivatives.—Cystine forms sparingly soluble salts with copper, $C_6H_{10}O_4N_2S_2Cu$; or mercury

$$C_6H_8O_4N_2S_2Hg_2,HgCl_2;$$
$$2C_6H_{10}O_4N_2S_2Hg,HgCl_2,7H_2O;$$
$$2C_6H_8O_4N_2S_2Hg_2,Hg(NO_3)_2.$$

With 30% nitric or hydrochloric acid (at room temperature) it yields compounds

$$C_6H_{12}O_4N_2S_2{\cdot}2HNO_3 \text{ and } C_6H_{12}O_4N_2S_2{\cdot}2HCl$$

(Mörner, Z. physiol. Chem. 1914, **93**, 203). *Cystine ethyl ester hydrochloride*,

$$S_2[CH_2{\cdot}CH(NH_2){\cdot}CO_2Et]_2,3HCl,$$

forms colourless needles, m.p. 185° with decomposition (Friedmann, Beitr. Chem. Physiol. Path. 1902, **3**, 1). Gortner and Hoffmann (J. Biol. Chem. 1927, **72**, 443) give 181° for the m.p. of *l-dibenzoyl cystine* and for *i*-, 170°. They also give the following derivatives of *l*- and *i*-cystine: *di-β-naphthalene sulphonyl l*-, 203–204°; *i*-, 215°; *phenyl*isocyanate *l*-, 148°; *i*-, 181°; *phenylhydantoin l*-, 122–123°; *i*-, 166°; *diethylester dihydrochloride l*-, 177°; *i*-, 185°. *l*-Cystine forms two sparingly soluble addition products with picric acid, one with 3 mols. and the other with 6 mols. cystine per mol. of picric acid (Toennies, Z. physiol. Chem. 1933, **222**, 1). Several other derivatives are described by Fruton and Clarke (J. Biol. Chem. 1934, **106**, 667). Numerous *acyl*- derivatives of cystine are described by Fischer and Suzuki (Z. physiol. Chem. 1905, **45**, 405; Fischer and Gerngross, Ber. 1909, **42**, 1485; Abderhalden and Wybert, Ber. 1916, **49**, 2449). Of these *di-l-leucyl-l-cystine*,

$$S_2[CH_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}CH(NH_2)C_4H_9]_2,$$

is a granular powder, turns yellow at 200°, and decomposes at a higher temperature, has $[a]_D^{20}$ −136·6°, or, when obtained in a crystalline form, has $[a]_D^{20}$ −141·4°; it gives a reddish-violet colour with copper sulphate; is precipitated by ammonium sulphate, and may be termed an *albumose*.

Mesocystine.—Loring and du Vigneaud (J. Biol. Chem. 1933, **102**, 287) describe the isolation of the internally compensated stereoisomer of cystine and give proof of its constitution. *Meso*cystine decomposes at 200–218°; *diformyl*- and *phenyluramino*- derivatives have m.p. 192–193° and 191°–192° respectively.

Loring, Dorfmann and du Vigneaud find that *meso*cystine can replace the natural *l*-cystine in the diet. *d*-Cystine does not promote growth. They suggest that *meso*cystine is reduced in the body with the liberation of *l*-cysteine (J. Biol. Chem. 1933, **103**, 399). The cystine isomerides also show differences in the ease with which they are oxidised to sulphate in the animal body (du Vigneaud Craft, and Loring, *ibid.* 1934, **104**, 81).

M. A. W. and W. V. T.

CYSTOPURIN. A compound of sodium acetate and hexamethylenetetramine (*Genatosan, Loughborough*). B.P.C. 1934.

CYTASE, as recently defined by Oppenheimer, is the group name for the enzymes which hydrolyse mannan, galactan, xylan and araban.

Xylan, which Haworth has shown to contain a chain of 18–20 xylopyranose units, is hydrolysed by the enzyme of *Helix*, giving 69% of xylose (Ehrenstein, Helv. Chim. Acta, 1926, **9**, 332) and by an enzyme in malt extract yielding 75% of xylose (Lüers, Woch. Brau. 1928, **45**, 83).

Mannan, galactan and araban are at present ill-defined substances, so that little can be said about their appropriate enzymes. Cytases are widely distributed, but with the exception of xylanase the statements about them are indefinite (*v.* BREWING, Vol. II, p. 87).

E. F. A.

CYTISINE. Cytisine is an alkaloid widely distributed in the Fam. Papilionaceæ; it has been isolated from different plants under various names (*ulexine*, *baptitoxine*, *sophorine*). Plugge and Plugge and Rauwerda (Arch. Pharm. 1895, **233**, 430; 1896, **234**, 685) have investigated between fifty and a hundred Papilionaceæ (*Cytisus*, *Ulex*, *Genista*, *Sophora*, *Baptisia*, *Euchresta*, *Anagyris*, spp.), and give the yields they obtained and a complete survey of the occurrence of cytisine. This list is completed by the work of Rauwerda (Chem. Zentr. 1898, I, 260). The yields vary considerably: *Cytisus Laburnum* (syn. *Laburnum vulgare*) contains roughly 1%; in *Sophora secundiflora* it may be as high as 3·47%. In *Anagyris fœtida* cytisine occurs together with anagyrine (*q.v.*), and N-*methyl-cytisine* (Ing, J.C.S. 1935, 1053). The latter has also been isolated from *Caulophyllum thalictroides* (Fam. Berberidaceæ) by Power and Salway (J.C.S. 1913, **103**, 191) and from *Thermopsis lanceolata* (syn. *Sophora lupinoides*) by Orechoff, Norkina and Gurewitsch (Ber. 1934, **67**, [B], 1394).

Extraction (Ing. J.C.S. 1931, 2195, with references concerning earlier extractions):—finely ground laburnum seeds (1 kg.) are intimately mixed with slaked lime (100 g.) and water (500 c.c.) is added; the mixture is then extracted with $CHCl_3$ for 20 hours. The solvent is evaporated *in vacuo*, the residue stirred with light petroleum and left overnight. Most of the alkaloid separates, the mother-liquor being extracted with dilute acid. The crude alkaloid is boiled in dilute HCl with animal charcoal, the filtered solution is made strongly alkaline and extracted with $CHCl_3$. The dried solution is evaporated, cytisine crystallising out at once (yield 20 g.). The alkaloid is best purified by distillation *in vacuo*, followed by crystallisation from dry acetone.

Cytisine (I), $C_{11}H_{14}ON_2$, $[a]_D^{17}$ −119° 57′ (in water, for further details concerning rotations, *see* Rauwerda, J.C.S. 1900, **78**, I, 607; Arch. Pharm. 1900, **238**, 477); m.p. 154·5–155·5°; b.p. 218°/2 mm.; crystallises from acetone in prisms. (I) is easily soluble in H_2O, EtOH, $CHCl_3$, but sparingly soluble in Et_2O and benzene.

N-*methyl*-(I), $[a]_D$ −234° 10′ (in H_2O), m.p. 136°, needles (from ligroin or acetone), is obtained by interaction of (I) and methyl toluenesulphonate (Freund and Gauff, Arch. Pharm. 1918, **256**, 33; *see also* Ing., *l.c.* 1931). N-methyl-(I)-methiodide, m.p. 276° (from MeOH).

N-*acetyl*-(I), m.p. 208° (Partheil, Arch. Pharm. 1892, **230**, 448); *mono*-N-*benzoyl*-(I) m.p. 116° (Maass, Ber. 1908, **41**, 1636); *p-toluenesulphonyl*-(I), m.p. 207–208°, soluble in dilute acid and warm **EtOH**, insoluble in cold **H_2O**, can be recrystallisod from hot **H_2O** (Ing., *l.c.*, 1931).

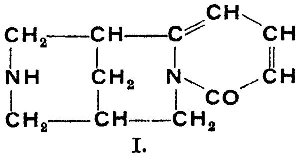
Treatment of (I) with **H_2O_2** yields *hydroxy-*(I) ,**$C_{11}H_{13}ON·NOH$**, m.p. 223–226° (Freund and Friedmann, Ber. 1901, **34**, 605). *Tetrahydrodeoxy-*(I), **$C_{11}H_{20}N_2$**, is formed by electrolytic reduction of (I), strongly alkaline oil, b.p. 270°/760 mm. (Freund and Horkheimer, Ber. 1906, **39**, 814).

In aqueous solution (I) or its salts gives a red colour with ferric salts, which is discharged by **H_2O_2**, a blue colour being eventually developed on heating (van de Moer's reaction, *see* Späth, Monatsh. 1919, **40**, 26).

Salts of (*I*).—(I) is a strong base and forms crystalline salts, the common salts are mono-acidic, but a dihydrochloride has been described (Partheil, *l.c.*, 1892), **$B·HCl,H_2O$**, colourless prisms; **$B·2HCl,3H_2O$**, yellow needles; **$B·HI,H_2O$**, yellow prisms; **$B_2·H_2SO_4$**, hygroscopic needles; **$B·HAuCl_4$**, reddish-brown needles, m.p. 220°, sparingly soluble in warm **H_2O**; **$B·HNO_3,H_2O$**, needles or leaflets, $[\alpha]_D$ - 81° 29′.

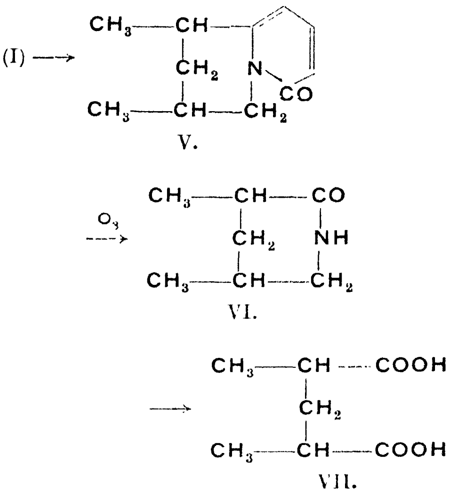
For dissociation constants of (I) and its salts, *v.* Kolthoff (Biochem. Z. 1925, **162**, 327).

Constitution of Cytisine (early references, *cf.* Ewins, J.C.S. 1913, **103**, 97, and Ing., *l.c.* 1931).—When (I) is heated with **HI** and red phosphorus to 230°, ammonia, *cytisoline* (II) (**$C_{11}H_{11}ON$**, needles from **EtOH**, m.p. 199°), and *β-cytisolidine* (III) (**$C_{11}H_{11}N$**, b.p. 132–133°/14 mm., platini-chloride, m.p. 234°) are obtained. (II) and (III) are reduced by sodium and **EtOH** to *α-cytisolidine* (IV), (**$C_{11}H_{15}N$**,, oil, platinichloride, m.p. 216°). Zinc dust distillation of (II) affords (III) (Freund, Ber. 1904, **37**, 16; Ewins, *l.c.*, 1913). Ewins (*l.c.* 1913) proved by synthesis (III) to be 6:8-dimethyl-quinoline and (IV) to be 6:8-dimethyl-1:2:3:4-tetrahydroquinoline; (II) is a hydroxy-6:8-dimethylquinoline. Späth (Monatsh. 1919, **40**, 93) showed that 2-hydroxy-6:8-dimethylquinoline is identical with (II). No further conclusions concerning the constitution of (I) can be drawn from these experiments. Van de Moer's colour reaction (*see above*) led Späth to conclude (*l.c.* 1919, p. 26) that (I) contains an α-pyridone group. Ing (*l.c.* 1931) first demonstrated that (I) does not contain a quinoline nucleus; from theoretical reasons and from the results of a Hofmann degradation he put forward a new formula for (I) which was but slightly modified by Späth and Galinovsky (Ber. 1932, **65**, [B], 1526) and accounts satisfactorily for all the degradation products of this compound.

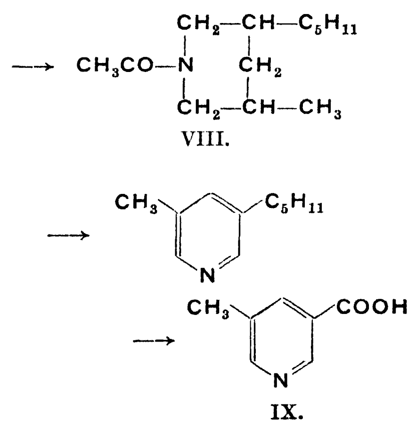


I.

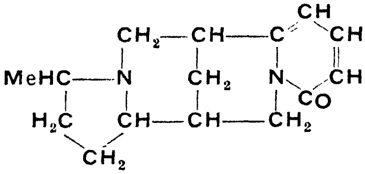
In the Hofmann degradation only the secondary N-atom is involved, the N-atom of the pyridone-system does not react. Späth and Galinovsky (*l.c.* 1932) demonstrated that hydrogenation of the des- bases after each interaction of alkali and quaternary base is essential so as to avoid polymerisation. These authors finally obtained *tetrahydro-hemicytisylene*, **$C_{11}H_{15}ON$** (V), which still contains all **C**-atoms of (I). By ozonolysis of (V), the adjacent pyridone ring is destroyed and a lactam **$C_7H_{13}ON$** (VI), formed which may be hydrolysed and then oxidised to a mixture of α-α′-dimethylglutaric acids (VII):



A further important proof for the correctness of formula (I) is provided by Ing (J.C.S. 1932, 2778) and by Späth and Galinovsky (Ber. 1933, **66**, 1338). The latter authors effected a Hofmann degradation on **N**-acetyl-tetrahydrodeoxy-(I), thus opening the reduced pyridone ring and leaving the other heterocyclic ring unattacked. The product obtained was **N**-acetyl-3-amyl-5-methylpiperidine (VIII), which was dehydrogenated and oxidised to *β*-methylnicotinic acid (IX).



(I) is closely related to the alkaloid anagyrine (*q.v.*).



Physiological Action.—(I) is a powerful poison resembling nicotine in its action (*cf.* Dale and Laidlaw, J. Pharm. Exp. Ther. 1911, **3**, 205). For toxicological identification, *see* Fühner and Mertens (Biochem. Z. 1921, **115**, 262); for microchemical identification of (I) in plant material, *see* Klein and Farkass (A. 1931, 243).

Schl.

CYTISOLIDINE *v.* Cytisine.

CYTISOLINE *v.* Cytisine.

CYTOCHROME. MacMunn in 1886 (Phil. Trans. **177**, 267) described a pigment, under the names myohæmatin and histohæmatin, which he found in muscles and other tissues of most animal species. He concluded that myo- and histo-hæmatin are respiratory pigments different from hæmoglobin and its derivatives. His observations were criticised by Hoppe-Seyler and others and although MacMunn made a strong defence, his views were not accepted, and his work was forgotten until 1925, when Keilin confirmed his discovery (Proc. Roy. Soc. B, 1925, **98**, 312). This worker found that the pigment was more widely distributed and more important than anticipated by MacMunn.

Keilin termed the pigment *cytochrome* and showed it to be an intracellular substance common to aerobic bacteria, yeast, higher plants and animals. Spectroscopic examination of cells showed it to exist in reduced and oxidised states. In the reduced state it shows, according to Keilin, a characteristic absorption spectrum composed of four bands, *a*, *b*, *c* and *d*, occupying practically the same position in most of the organisms studied. In the muscles of guinea-pigs, for instance, the bands are found at (*a*) 6045Å, (*b*) 5662Å, (*c*) 5500Å, (*d*) 5205Å, whilst the positions of maximum intensity of the bands in the thoracic muscles of bees are (*a*) 6046Å, (*b*) 5665Å, (*c*) 5502Å, (*d*) 5210Å.

The absorption spectrum markedly alters on oxidation, the four strong bands disappearing and being replaced by weak diffuse bands lying about *α* 5665Å and *β* 5287Å. The highest concentration of the pigment is found in actively metabolising tissues such as the thoracic wing muscles of flying insects, heart muscles of mammals or birds, pectoral muscles of flying birds or in baker's yeast.

There is some parallelism between the concentration of cytochrome in cells and their respiratory activities. The pigment is apparently completely absent from anaerobic organisms.

It was shown by Keilin that cytochrome is not one chemically defined substance but a mixture of three hæmochromogen-like compounds, *a′*, *b′*, and *c′*, capable of being oxidised and reduced independently of each other. The bands *a*, *b*, and *c* of cytochrome represent the *α*-bands of the three corresponding compounds, whilst the band *d* represents the fused *β*-bands of at least the two compounds *b′* and *c′*.

The characteristic properties of cytochrome components are due to the nitrogenous compounds with which their hæmatins are combined. "Cytochrome components differ from their hæmatins just as much as hæmoglobin differs from hæmatin" (Keilin). Certain variations in the structure and properties of cytochrome are revealed by the study of micro-organisms (Keilin, Nature, 1934, **133**, 290). Whilst the absorption spectrum of cytochrome is usually similar to that of bakers' yeast (*a* 6030Å, *b* 5650Å, *c* 5500Å, *d* 5230Å) the bands *b* and *c* may be replaced by a single band b_1 (*e.g.* in *B. Coli*, *B. proteus*, *B. megatherium*, b_1= 5600Å), or band *a* may be shifted a little either towards the violet or the red. It can be definitely stated that the three components of cytochrome "represent three distinct hæmochromogen compounds each having at its base a different Fe-porphyrin nucleus. It is possible that these Fe-porphyrin nuclei are united to similar if not identical nitrogen compounds. These components may also differ in the degree of their dispersion."

Of the three components of cytochrome two, *b′* and especially *a′*, are very unstable; they are as fragile as most of the enzymes (Keilin, Ergeb. d. Enzymforschung, 1933, II, 239). Component *a′* decomposes at 55°C., liberating its hæmatin compound. Component *c′* is heat stable and may be easily extracted from baker's yeast. Keilin has studied the relationship of cytochrome to respiratory enzymes of the cell (Proc. Roy. Soc. 1929, **104**, B. 206). His conclusions are as follows: (1) Components *a′* and *c′* of cytochrome are not autoxidisable, whilst *b′* and an unbound hæmatin also found in the cell are autoxidisable. The latter in the reduced state can combine with carbon monoxide. (2) The hæmochromogen precursor of cytochrome is also autoxidisable but cannot combine with carbon monoxide. (3) Constituents of cytochrome can give rise to thermostable peroxidase activity. (4) The indophenol oxidase of cells (which is inhibited by cyanide or carbon monoxide) is responsible for the oxidation of cytochrome, especially of its non-autoxidisable components *a′* and *c′*. (5) Cytochrome in living cells is reduced by organic compounds, especially succinic acid, when these are activated by their dehydrogenases. (6) Cytochrome acts as a hydrogen carrier between activated organic compounds and activated oxygen. (7) The autoxidisable component *b′* may act as a carrier between similar activated molecules and free molecular oxygen.

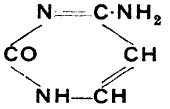
Keilin (Proc. Roy. Soc. 1930, **106**, B, 418) has described a method of extracting cytochrome *c′* from bakers' yeast. This consists of plasmolysing Delft yeast with NaCl and pouring into boiling tap water. The mixture, after standing a short time, is cooled with ice, allowed to settle, the supernatant fluid removed, and the deposit of yeast filtered on a Buchner funnel and washed. The yeast cakes so formed are suspended in a solution of sodium bisulphite, sodium hyposulphite ($Na_2S_2O_4$) is added, and the mixture is left overnight in a stoppered bottle. The clear pink filtrate contains, in solution, cytochrome *c′*, mixed with salts and proteins. Subsequent treatment with $CaCl_2$ and SO_2 effects a separation of the pigment.

The component *c′* thus extracted corresponds to the modified myohæmatin of MacMunn and shows two strong bands in the visible spectrum, *α* at 5495Å and *β*, which seems to consist of three maxima, the central one of which is approximately at 5200Å. Dixon, Hill and Keilin (Proc. Roy. Soc. 1931, **109**, B, 29) find that the absolute absorption spectrum of reduced cytochrome *c′* in the violet belongs to the type of spectrum given by hæmatin compounds. The spectrum of cytochrome *c′* in the reduced state is that of a typical hæmochromogen and in the oxidised state that of a parahæmatin compound. Reduced cytochrome *c′* does not oxidise in neutral solution; at p_H 4 and at p_H 13 it becomes, however, autoxidisable. It reacts with carbon monoxide under alkaline conditions, forming a compound easily dissociated by light—behaving thus like an autoxidisable hæmochromogen. “It differs from all known hæm and hæmochromogen compounds which on shaking with air rapidly oxidise to the corresponding hæmatin and parahæmatin compounds.” The constitution of the hæmatin of cytochrome *c′* is as yet unknown (Roche and Bénévent, Compt. rend. Soc. Biol. 1936, **123**, 18). Reduced cytochrome is not oxidised by iron compounds, but by H_2O_2, ferricyanide, and copper salts. Oxidised cytochrome is reduced by sodium hyposulphite, cysteine, *p*-phenylenediamine, and catechol. Its reduction in the living cell is accomplished by activated hydrogen donators (metabolites), the reduced form being oxidised through the indophenol oxidase. Hence its oxidation in the cell can be inhibited by substances which poison the indophenol oxidase, *e.g* cyanide, or H_2S. Under anaerobic conditions cytochrome is found in the living cell in the reduced form which then shows the typical spectrum. Removal of the anaerobic state under normal conditions (*e.g.* shaking with air or oxygen) causes oxidation of the reduced form of the pigment and the disappearance of the characteristic spectrum. This phenomenon may be observed in living tissues. Recent work (*e.g.* by Theorell, Biochem. Z. 1935, **279**, 463; 1936, **285**, 207) has emphasised the important part played by cytochrome as a carrier in the respiration of aerobic cells.

Further information may be sought in an article by Shibata, which deals particularly with bacterial cytochrome (Ergeb. d. Enzymforschung. 1935, IV, 348) and in the papers of Keilin and his colleagues.

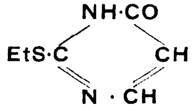
J. H. Q.

CYTOSINE, 2-oxy-6-amino-dihydropyrimidine,

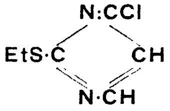


Keto-form.

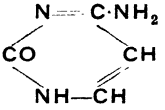
a product of hydrolysis of the nucleic acid from the thyroid gland and of nucleic acids of other origin. It has been synthesised by the following series of reactions: *ψ*-ethylthiocarbamide hydriodide and ethyl sodioformylacetate condense to form 2-*ethylthiol*-6-*oxydihydropyrimidine*



which is converted by the action of phosphorus pentachloride into 2-*ethylthiol*-6-*chloropyrimidine*



this reacts with alcoholic ammonia to form the 6-*amino*-derivative, which yields on prolonged boiling with hydrobromic acid, 2-*oxy*-6-*amino-dihydropyrimidine*



identical with natural cytosine (Wheeler and Johnson, Amer. Chem. J. 1903, **29**, 492, 505; Hilbert and Johnson, *ibid.* 1930, **52**, 1152).

Cytosine crystallises with one molecule of water in thin colourless pearly plates, becomes anhydrous at 100° and decomposes at 320–325°. It is insoluble in ether, and sparingly soluble in alcohol or water, 1 part dissolving in 129 parts of water at 25°.

D.

DAHL'S ACIDS, I, 2-naphthylamine-5-sulphonic acid; II, 1-naphthylamine-4:6-disulphonic acid; III, 1-naphthylamine-4:7-disulphonic acid.

DAMASCENINE, methyl 2-methylamino-3-methoxy benzoate, $C_{10}H_{13}O_3N$, m.p. 25–26°, b.p. 154°/15 mm., 270°/750 mm., occurs in the seeds of *Nigella damascena* (Linn.) (0·4–0·5%) and of *N. aristata.*

Its constitution was established by synthesis (Ewins, J.C.S. 1912, **101**, 544) and “methyl damascenine” (Keller, Arch. Pharm. 1908, **246**, 1), shown to be identical with damascenine: damasceninic acid, $C_9H_{11}O_3N$, stated by

Pommerehne (*ibid.* 1900, **238**, 531) to be isomeric with damascenine, is a product of hydrolysis of the alkaloid (*see also* Keller and Schulze, *ibid.* 1925, **263**, 481). An alternative method of synthesis has been described by Kaufmann and Rothlin (Ber. 1916, **49**, 578). A full account of the properties and synthesis of damascenine, which is also described as the odoriferous principle of oil of Nigella used in perfumery, is given by Sornet (Manf. Chem. 1924, **5**, 87).

Damascenine is mildly narcotic in action.

A. J. E.

DAMBONITOL, m.p. 195°, is a dimethyl ether of *i*-inositol; it is found in Gabon rubber and in the latex of *Castilloa elastica.*

E. F. A.

DAMMAR RESIN. The word used in the Malay States is damar, indicating resin used for making torches. The word "dammar" is here restricted to the resin used in spirit varnishes and nitrocellulose lacquers, etc., which is obtained from various species of the *Dipterocarpaceæ* and possibly *Burseraceæ.* The trees producing these resins are found on the Malayan Peninsula and the Pacific islands generally. For a full account of the dammar resins obtained in the Federated Malay States and the Straits Settlements, from which the greater part of the world's supply comes, reference should be made to a report by the Conservator of Forests, F.M.S. and S.S. (*see* J. Oil Col. Chem. Assoc. 1924, **7**, 186). The resin is obtained by a tapping process, somewhat similar to that used in the production of ordinary turpentine. One of the highest grades of dammar is that known as Cat's Eye dammar, the finest pieces of which yield an almost colourless solution in coal tar hydrocarbons. It is mostly obtained from species of *Hopea*, principally *H. micrantha.* The tree exudes resin, which congeals on the trunk. This particular type of tree will not yield a steady supply by tapping. In the Malay States this is known as Mata Kuching. From the commercial point of view dammar known as Penak or damar Penak is more important in regard to quantity, although it is not of as high a quality as Mata Kuching. Penak is the product of *Balanocarpus Heimii.*

Three samples of dammar examined at the Imperial Institute were found to have the following characters.

	1. Pale lumps.	2. Brownish-yellow.	3. Pale powder.
Moisture, % . .	0·6	0·7	1·1
Extraneous matter, %	0·2	0·1	2·8
Acid value . . .	35·1	34·6	38·3
Saponification value	39·6	38·1	47·8
Ash, %	0·01	0·01	1·61
Softening-point °C. .	71	80	72
Temp. of gradual fusion °C. . . .	83–95	88–98	80–90

The difficulty in adopting limit figures for this resin is shown by the fact that acid values up to 72 have also been found by the Imperial Institute.

Coffignier (Bull. Soc. chim. 1911, [iv], **9**, 549) gives the following figures for six samples of known origin:

	1	2	3	4	5	6
Sp.gr. at 18° . .	1·036	1·048	1·057	1·025	1·004	1·032
Melting-point . .	95°	120°	95°	110°	190°	105°
Acid value . . .	31·4	35·1	30·1	19·9	59·6	18·5
Saponification value	33·7	64·5	39·3	30·9	64·5	19·6
Insoluble in alcohol, %	20·3	23·6	19·1	22·4	45·5	32·8
Insoluble in ether, %	4·5	9·6	1·0	4·1	37·9	3·2
Insoluble in acetone %	14·7	20·4	14·0	16·4	45·3	21·3

Origin.—1. Padang. 2. Borneo. 3. Singapore.
4. Pontianac. 5. Sumatra. 6. Batyan.

Barry ("Natural Varnish Resins," p. 106 *et seq.*) gives analyses of a number of samples which are of considerable value, as the samples were supplied by the Conservator of Forests, F.M.S. and S.S. The samples included Dammar Mata Kuching, Penak, "dead" dammar, and some inferior dammars. For Mata Kuching he found acid values 21·5, 23·2, and 23·8, and from 0·05–0·47% insoluble in chloroform. For Penak, acid values 34–37·1, and from 0·2–3·64% insoluble in chloroform. The high figures for insoluble matter were found for samples in powder form and may therefore merely indicate high extraneous matter. A sample of Dammar Temak gave the following results:

Acid value	20·6
Saponification value .	25·6
Loss at 105° . . .	1·06%
Melting-point . . .	80–90°
Iodine value (Wijs) .	61

Dead dammar, a name applied to the opaque resin, sometimes yielded by *Balanocarpus Heimii*, gave the following figures:

	1.	2.	3.
Moisture (at 105°), % .	0·67	5·86	2·5
Insoluble in $CHCl_3$, %	1·76	Traces	0·65
Ash, %	0·04	0·12	0·19
Acid value	30·5	26·7	28·4
Non-resinous matter, %	2·4	5·98	3·32
Acid value of pure resin	31·3	28·4	29·0

Two samples of Siamese dammars have been examined by F. H. Geake (Ind. Eng. Chem. 1927, **19**, 826), both of which were probably from species of *Shorea.* They had the following characters:

	1.	2.
Specific gravity . . .	1·059	1·055
Acid value	32·9	18·2
Saponification value . .	159·2	44·9
Moisture, %	1·9	0·8
Ash, %	0·14	0·35
Softening-point . . .	145°	75°
Melting-point	193°	85°

Three samples of Siamese resin examined by Barry (*op. cit.*) gave acid value 17·4–27, saponification value 26·2–45·5, iodine value (Wijs) 43·5–60, insoluble in chloroform 0·4–2·58%.

It is not considered wise to include the suggested composition of this resin, as the results of combustions giving formulæ such as $C_{56}H_{80}O_8$ to a resin acid can hardly be relied on until crystalline derivatives are prepared (*see* Dulk, J. pr. Chem. 1848, [i], **45**, 16).

A so-called Borneo dammar is obtained from *Vatica moluccana*. Kemner (Farben-Ztg. 1936, **41**, 586) states that it has acid value 13·47, saponification value 60·37, and melting-point 200°. It contains a little wax, which causes its solutions to be somewhat cloudy. It is known as Hiroe dammar.

E. J. P.

DANAITE. A cobalti-ferrous variety of mispickel (ironsulpharsonide, $FeAsS_2$), 4–10% cobalt replacing iron.

DANALITE. A rare sulpho-silicate mineral, with the formula $3R_2SiO_4 \cdot RS$, where R represents Fe, Zn, Be, Mn, containing BeO about 14%. The flesh-red or grey cubic crystals are octahedral or tetrahedral in habit; sp.gr. 3·35–3·43; H.=5½–6. It occurs in granite at Rockport and Gloucester, in Massachusetts, and large crystals have been found in Cornwall. Closely allied is the tetrahedral-cubic mineral *helvite*, which contains about the same amount of beryllium, but with a preponderance of manganese and no zinc.

L. J. S.

DANDELION, *Taraxacum officinale* Wiggers (Fam. Compositæ). A common weed of Europe and America. The leaves, which have a somewhat bitter taste, are sometimes eaten after boiling or used green as a salad. For this latter purpose they are frequently blanched. Recorded analyses of edible leaves are: water, 85·5%; protein, 2·4–2·8%; fat, 0·7–1·0%; N-free extract, 7·5–10·6%; fibre, 1·5%; ash, 2·0%. According to J. S. Kleiner and H. Tauber (Science, 1935, **82**, 552) the ascorbic acid content of leaves averages 0·08–0·10 mg. per g. of fresh material. The "down" of dandelion seeds contains, in addition to cellulose, soluble pentoses, hemicellulose and probably a xylan (Votoček and Zvoníček, Coll. Czech. Chem. Comm. 1933, **5**, 448). Karrer and Schöpp have isolated a flavin from alcoholic extracts of the flowers (Helv. Chim. Acta, 1934, **17**, 771).

A. G. Po.

DAPHNANDRA ALKALOIDS. The bark of the Australian plant *D. repandula* (Fam. Monimiaceæ) is remarkably rich in total alkaloids (6%). Pyman (J.C.S. 1914, **105**, 1679) isolated and characterised three new alkaloids from *D. micrantha*: *daphnandrine* (I) (1·5–2%), *micranthine* (II) (max. 0·5%), and *daphnoline* (III) (1·5%). Mode of extraction: ground bark percolated with 0·25% aqueous tartaric acid, concentrated, made alkaline with NH_3, and extracted with $CHCl_3$. Separation of phenolic from non-phenolic bases by shaking $CHCl_3$ extract with NaOH. $CHCl_3$ evaporated and residue treated with $CH_3 \cdot CO_2Et$, when crude (I) separated. The residue is a mixture of (I) and (II) and is finally separated by conversion into the oxalates. The phenolic portion (*see above*) is acidified, made alkaline with Na_2CO_3 and (III) taken up in $CHCl_3$, from which solution the crude phenolic base soon separates.

Daphnandrine (I), $C_{36}H_{38}O_6N_2$, colourless needles from $CHCl_3$, with 0·5 mol. solvent of crystallisation, m.p. 280°, $[\alpha]_D$ +474·7° (anhydr.) practically insoluble in boiling H_2O, and all organic solvents except boiling $CHCl_3$. The base contains three OMe and one NMe groups. Hydrochloride, $B \cdot 2HCl + 5H_2O$, colourless prisms, m.p. 282° (anhydr.), $[\alpha]_D$ +296–314°; hydrobromide $B \cdot 2HBr + 6H_2O$, m.p. 291° (anhydr.), $[\alpha]_D$ +265–280°; acid oxalate, $B \cdot 1\frac{1}{2}H_2C_2O_4 + 5\frac{1}{2}H_2O$, m.p. 225°.

Micranthine (II), $C_{36}H_{32}O_6N_2$, colourless needles from $CHCl_3$, m.p. 190–196°. The base contains one OMe and one NMe group. Insoluble in H_2O and Et_2O, sparingly soluble in EtOH or $CHCl_3$, the only crystalline salt is the sulphate $B \cdot H_2SO_4 + 10H_2O$, fine colourless needles (from H_2O) decomposing at 312°.

Daphnoline (III),

$$C_{34}H_{34}O_6N_2 \text{ or } C_{35}H_{36}O_6N_2,$$

crystallises from $CHCl_3$ or EtOH in small hexahedra with solvent of crystallisation, m.p. 190–215°, $[\alpha]_D$ +459° (dry base in $CHCl_3$); (III) is even less soluble in organic solvents than (I). Hydrochloride $B \cdot 2HCl + 3\frac{1}{2}H_2O$, large truncated bi-pyramids, from moist EtOH, m.p. 290° (anhydr.), $[\alpha]_D$ +283°. The base contains two OMe and one NMe groups. Hydrobromide $B \cdot 2HBr + 4H_2O$, clusters of microscopic needles, readily soluble in hot but sparingly so in cold H_2O, m.p. 286° (anhydr.).

The three alkaloids give characteristic colour reactions with Fröhde's reagent: (I) indigo changing to port-wine red; (II) indigo changing to emerald green; (III) violet changing to port-wine red.

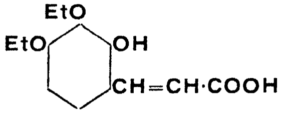
There is nothing known about the constitution of the three alkaloids, for further colour reactions and pharmacological action, *v.* Pyman (*l.c.*).

Schl.

DAPHNETIN. Daphnetin is present in the form of its glucoside, *daphnin*, in the bark of the *Daphne alpina* Linn., *D. Mezereum* Linn., and *D. odora* (Thunb.).

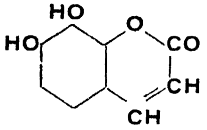
The concentrated alcoholic extract is digested with boiling water, filtered and treated with lead acetate solution. The precipitate is removed, basic lead acetate added to the filtrate, the lead compound of the glucoside decomposed with hydrogen sulphide, and the solution evaporated (Zwenger, Annalen, 1860, **115**, 8). When hydrolysed with boiling dilute acids, daphnin yields daphnetin and glucose.

Daphnetin, $C_9H_6O_4$, pale yellow needles, m.p. 256°, is soluble in alkalis with a yellow colour, and gives a yellow precipitate with lead acetate solution. It forms a *monoethyl ether*, colourless plates, m.p. 155°, and a *diethyl ether*, needles, m.p. 72°. When the latter is boiled with caustic soda solution, the *diethyl ether* of *daphnetinic acid*:



is produced, and this, by ethylation, yields the *triethyl* derivative. Oxidation of daphnetinic acid triethyl ether gives triethoxybenzaldehyde, which is readily converted into triethoxybenzoic acid. The silver salt of this acid, when destructively distilled, yields pyrogallol triethyl ether.

Daphnetin is accordingly 7:8-dihydroxycoumarin:



(Stünkel, Ber. 1879, **12**, 109; Will and Jung, *ibid.* 1884, **17**, 1081).

It has been synthetically prepared by heating pyrogallol with malic acid in the presence of sulphuric acid (von Pechmann, *ibid.* 1884, **17**, 933), and by the condensation of pyrogallaldehyde with sodium acetate (Gattermann and Koebner, *ibid.* 1899, **32**, 287).

The following derivatives have been prepared:

Dibenzoyldaphnetin, m.p. 152°; *diacetyldaphnetin*, needles, m.p. 129° (von Pechmann, *l.c.*), m.p. 137° (Asai, Acta Phytochim. 1930, **5**, 9).

8-*Hydroxy*-7-*methoxycoumarin*, m.p. 175°; 8-*hydroxy*-7-*ethoxycoumarin*, m.p. 145°; 8-*methoxy*-7-*ethoxycoumarin*, m.p. 81°; and 7-*methoxy*-8-*ethoxycoumarin*, m.p. 85·5° (Wessely and Sturm, Ber. 1929, **62**, [B], 115; 1930, **63**, [B], 1299).

Ethyl daphnetin-3-*carboxylate*, m.p. 231–232° (*diacetyl* derivative, m.p. 129–130°), and the corresponding *acid*, m.p. 263° (*diacetyl* derivative, m.p. 213–214°) (Boehm, Arch. Pharm. 1933, **271**, 490).

Daphnetin-3-*carboxylic acid*, m.p. 228°; 8-*hydroxy*-7-*acetonyloxycoumarin*, m.p. 132–133°; and 8-*methoxy*-7-*acetonyloxycoumarin*, m.p. 81–82° (Rây, Silooja, and Vaid, J.C.S. 1935, 813).

4-*Methyldaphnetin* and its derivatives (Sakai and Kato, J. Pharm. Soc. Japan, 1935, **55**, 691).

Daphnetin is a yellow colouring matter and gives very pale yellow, pale olive-yellow, olive-yellow, and olive-black shades on wool mordanted with tin, aluminium, chromium and iron respectively (Perkin and Wilson, J.C.S. 1903, **83**, 134).

Daphnin, $C_{15}H_{16}O_9$, colourless prisms, m.p. 228–229°, dissolves in alkaline solutions with a yellow colour. Methylation of daphnin and subsequent removal of the sugar group (Wessely and Sturm, *l.c.*) yield 7-*hydroxy*-8-*methoxycoumarin*, m.p. 185·5°. Daphnin, therefore, contains the glucose residue in position 7, and is not identical with the daphnetin glucoside synthesised by Leone (Gazzetta, 1925, **55**, 673) from β-acetobromoglucose and daphnetin.

According to Asai (*l.c.*), the amount of daphnin present in various parts of the *D. odora* varies with the season, *e.g.* large quantities are present in the leaf-buds in the early stages of development. Daphnin absorbs short waves, especially between the frequencies 3,200 and 3,900, and in this respect is similar to flavone. Coumarin and hydroxycoumarin glucosides resemble the hydroxyflavones in their light absorption and localisation in plants, and probably serve the same physiological purpose.

A. G. P. and E. J. C.

DAPHNIN *v.* DAPHNETIN.

DAPHNOLINE *v.* DAPHNANDRA ALKALOIDS.

D'ARCET'S ALLOY *v.* BISMUTH (Vol. I, p. 698).

DARCO *v.* ADSORPTION.

DARWINITE. A copper arsenide, similar to Domeykite, Cu_3As.

DATE. The fruit of the palm *Phœnix dactylifera.* Dates form the historic food of the Arabs, and in recent times have been cultivated in southern areas of the United States. Varieties imported into Europe are usually soft-fleshed and sticky. "Dry," firmer types are more common around desert habitations. Attwater and Bryant (U.S. Dept. Agric. Off. Exp. Sta. Bull. 1906, No. 28) give the average percentage analysis of the edible flesh of cured dates as: water 15·4, protein 2·1, fat 2·8, N-free extract + fibre 78·4, ash 1·3. The soluble carbohydrates of the date consist largely of sucrose, the Deglet Noor (Sahara) variety containing exceptionally large proportions. Fattah and Cruess (Plant Physiol. 1927, **2**, 349) record that Mesopotamian varieties contain larger proportions of total solids and of sugars than the American-cultivated types. In many varieties the actual sucrose content is higher in the green than in mature fruit, and 20–25% may be inverted before harvesting. Approximately 3% of the carbohydrates are in the form of pentosans (Wittmann, Z. landw. Versuchs. Oesterreich, 1901, **4**, 131, and according to Reif (Z. Unters. Lebensm. 1934, **68**, 179) a small amount of sorbitol is also present. A. R. C. Haas and D. E. Bliss (Hilgardia, 1935, **9**, No. 6, 295) report a detailed study of the growth and composition of the Deglet Noor variety.

Dried ground date stones have the percentage composition: water 7·96, ash 0·89, protein 5·25, carbohydrates 65·53, fibre 13·60, oil 6·77. The oil has the following characteristics: $d^{15\cdot5}$ 0·9201, n_D^4 1·4580, saponification value 206·1, iodine value 54·5, unsaponifiable matter 1·98%, free acid (as oleic) 0·5%, Reichert-Meissl value 1·0, Polenske value 3·0, insoluble fatty acids (m.p. 22°) 88·7% (R. G. Harry, Analyst, 1936, **61**, 403).

The dried, roasted and ground stones have been utilised as a coffee substitute, analysis of which shows:

	H_2O	Protein.	Fat.	N-free extract.	Fibre.	Ash.
	%	%	%	%	%	%
American	5·5	6·7	11·2	59·0	15·8	1·75
German	6·6	5·5	7·9	50·9[1]	27·8	1·3

[1] Includes 2·2% of sugar.

The sap of the date palm collected from incisions made in the bark has a high sugar content, and after clarification and evaporation yields a crude brown sugar or jaggery.

An Indian beverage prepared from dates is stated by Biswas and Guha (Indian Med. Gaz. 1935, **20**, 382) to have ten times the vitamin-C content of cows' milk, and a considerable proportion of vitamin-B.

According to Das and Sarin (Ind. Eng. Chem. 1936, **28**, 814) vinegar may be satisfactorily prepared from aqueous extracts of dates by inversion of the sugar with acid, and subsequent fermentation; 100 lb. of fresh fruit are stated to yield 12–15 gals. of standard vinegar.

A. G. Po.

DATILE. The fruit of *Muntingia Calabura.* This is a native of southern United States and is also grown in the West Indies. The small, round fruits (1·5 cm.) comprise a firm epicarp enclosing a mass of pulp and seeds.

Pratt and del Rosario (Philippine J. Sci. 1913, **8**, 59) record the percentage analysis of the edible pulp and seeds as: total solids, 24·6, insoluble solids 8·4, protein 2·0, acids, as malic, 0·1, reducing sugar 8·1, sucrose 5·3, ash 0·8%.

A. G. Po.

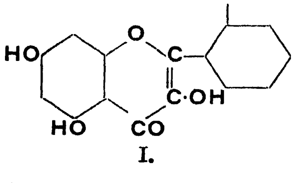
DATISCA CANNABINA *Linn.* This is a tall, erect herb, resembling hemp, belonging to the Datisceæ and met with in the temperate and sub-tropical western Himalayas from Kashmir to Nepal. The root, known as *Alkalbir,* has been extensively used in Kashmir and throughout the Himalayas as a yellow dyestuff, chiefly on alum-mordanted silk; but the colouring matter appears to be present in the whole plant as the leaves and twigs can also be employed for the same purpose.

From the leaves of the *Datisca cannabina,* Braconnot (Ann. Chim. 1816, [ii], **3**, 277) isolated a crystalline substance which he termed *datiscin.* It was subsequently shown by Stenhouse (Annalen, 1856, **98**, 166) that this compound is a glycoside which on hydrolysis yields a sugar and a yellow colouring matter, *datiscetin,* $C_{15}H_{10}O_6$.

Schunck and Marchlewski (Annalen, 1893, **277**, 261) suggested the formula $C_{15}H_{12}O_6$, and showed that, on fusion with alkali, datiscetin gives salicylic acid. By the action of dilute nitric acid, a nitrosalicylic acid was obtained, whereas with strong nitric acid, picric acid was formed. Datiscetin appeared to contain methoxyl groups, and was considered by the authors to be most probably a xanthone derivative.

On the other hand, Korczyński and Marchlewski (Chem. Zentr. 1906, II, 1265; 1907, II, 700; Biochem. Z. 1907, **3**, 295) show that pure datiscetin, $C_{15}H_{10}O_6$, does not contain methoxyl groups. It is soluble in alkaline solutions with a yellow colour, and gives with sulphuric acid a yellow liquid possessing a green fluorescence. When boiled with concentrated solutions of alkalis, phenol and salicylic acid are produced.

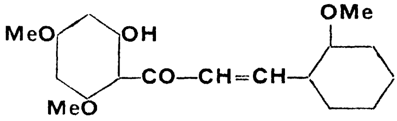
By the action of bromine on a solution of datiscetin in boiling acetic acid, Leskiewicz and Marchlewski (Ber. 1914, **47**, 1599) obtained tribromophloroglucinol, and as a result suggested that this colouring matter is 5:7:2′-trihydroxyflavonol (I). This conclusion was confirmed by Kalff and Robinson (J.C.S. 1925, **127**, 1968), who synthesised datiscetin by the action of *o*-methoxybenzoic anhydride and sodium *o*-methoxybenzoate on ω-methoxyphloracetophenone at 180°, and hydrolysis of the product. The datiscetin 3:2′-dimethyl ether thus obtained yielded, on demethylation, datiscetin (I), pale yellow needles, m.p. 276° (corr.), identical with the natural product. From an examination of the actual specimen of datiscetin isolated by Schunck and Marchlewski (*l.c.*), Kalff and Robinson conclude that the specimen consists essentially of datiscetin mixed with galangin.



I.

Tetracetyldatiscetin, colourless prisms, m.p. 141° (corr.), and *tetrabenzoyldatiscetin,* colourless needles, m.p. 191–192° (corr.), are described.

Bargellini and Peratoner (Gazzetta, 1919, **49**, 64) prepared datiscetin 5:7:2′-trimethyl ether from 2-hydroxy-4:6:2′-trimethoxyphenyl styryl ketone (II), which, by means of dilute alcoholic hydrochloric acid, yields the corresponding flavanone. The *iso*nitroso- derivative of the latter, when heated with hydrochloric acid in acetic acid solution, is converted into 5:7:2′-*trimethoxyflavonol,* pale yellow needles, m.p. 158–160°, which gives with sulphuric acid an intensely green fluorescent solution.



II.

Datiscin.—According to Charaux (Compt. rend. 1925, **180**, 1419), datiscin, $C_{27}H_{30}O_{15},4H_2O$, m.p. 192–193°, $[\alpha]_D$ −48·6° in alcohol, occurs to the extent of 6–10% of the dry weight of the roots and leaves of the *Datisca cannabina.* It is hydrolysed by enzymes yielding equimolecular amounts of datiscetin and a rhamnoglucose, *rutinose* (*cf. ibid.* 1924, **178**, 1312; Zemplén and Gerecs, Ber. 1935, **68**, [B], 1318). By hydrolysis with acids, datiscin gives 1 mol. of datiscetin, 1 of dextrose, and 1 of rhamnose.

Dyeing Properties of Datisca cannabina.—The dyeing properties of datisca root on wool are very similar to those of Old Fustic. It is, however, slightly inferior in dyeing power. On cotton it dyes more like quercitron bark, in so far that the olives obtained on iron mordant are bluer in shade, as though some tannin matter were present. It appears to have about the same colouring power as quercitron bark, but gives a brighter yellow with aluminium mordant (Hummel and Perkin, J.S.C.I. 1895, **14**, 458).

A. G. P. and E. J. C.

DATISCETIN AND DATISCIN *v.* Datisca Cannabina.

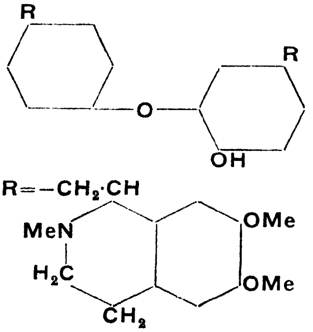
DATOLITE. A native borosilicate of calcium, $HCaBSiO_5$, containing B_2O_3 21·8%. Monoclinic crystals, with a profusion of small brilliant faces, many with five-sided outlines, are of common occurrence; these are usually transparent and colourless, or with a faint greenish tinge; sp.gr. 3·0. The mineral most often occurs associated with zeolites in the amygdaloidal cavities of basaltic rocks, *e.g.* in the neighbourhood of Edinburgh and Glasgow, and at Bergen Hill and West Paterson in New Jersey. It, however, presents several other modes of occurrence: viz. in granite at Baveno in Piedmont ; in diorite at Rosskopf in Baden; in gabbro with copper ores at Monte Catini in Tuscany; in "limurite" (an axinite-pyroxenite) at Dundas in Tasmania; in serpentine in the Lizard district in Cornwall ; in calcite veins in sandstone at Sonthofen in Bavaria ; in veins of silver ore at Andreasberg in the Harz Mountains ; in the Lake Superior copper mines (here as a compact, opaque, white form resembling unglazed porcelain); in beds of magnetite in gneiss at Arendal in Norway.

L. J. S.

DATURA STRAMONIUM, a bushy annual plant, growing in the warmer temperate regions. The seeds and leaves contain about 0·1 to 0·5% of alkaloid (*daturine*), consisting of hyoscyamine associated with small quantities of atropine and hyoscine.

DATURINE *v.* DATURA STRAMONIUM.

DAURICINE, $C_{38}H_{44}N_2O_6$, isolated from *Menispermum dauricum* (1·3%) by Kondo and Narita (Amer. Chem. Abstr. 1927, **21**, 2700). Slightly yellow, amorphous base, m.p. 115°, $[\alpha]_D^{11}$ −139°, soluble in $EtOH$, acetone, benzene, and Et_2O. *Dimethiodide* needles, m.p. (anhydr.) 204°, $[\alpha]_D^{22}$ −110°, O-*methyldauricindimethiodide* prisms, m.p. 152° (decomp.); $[\alpha]_D^{22}$ −80·1. For absorption-spectrum, *see* Ochiai (Amer. Chem. Abstr. 1929, **23**, 5272). Faltis and Frauendorfer (Ber. 1930, **63**, 809) first suggested that dauricine belongs to the group of the *bis*-coclaurine-alkaloids (*q.v.*) (*see also* von Bruchhausen and Gericke, Arch. Pharm. 1931, **269**, 115), which suggestion has finally been proved by the synthesis of methyl-dauricine-α-methine, m.p. 125–126° (Kondo, Narita, and Uyeo, Ber. 1935, **68**, 519 ; for complete survey, *see also* Kondo, Arch. Pharm. 1936, **274**, 65). Dauricine has the following constitution :



Schl.

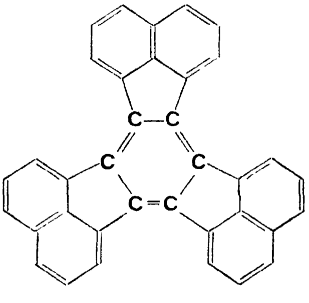
DAVITAMON. Trade name for preparations containing vitamin A, D, or both (*Organon Laboratories, London*). B.P.C. 1934.

DEAD DIPPING. The process of producing a pale yellow dead surface on ornamental brasswork. The brasswork, after the final stamping, with its adhering black scale from the annealing oven, is placed in dilute nitric acid until the scale is detached, when it is removed and washed with water. It is next plunged into stronger nitric acid, and when its surface is covered with minute gas bubbles, it is washed in a solution of argol and dried in hot sawdust.

DEAD OIL. The higher boiling fractions of shale oil, from which the greater portion of the solid paraffin has been removed by crystallisation.

DECACYCLENE, $C_{36}H_{18}$, formed when acenaphthene is heated alone, with sulphur, or (for greatest yield, 30–35%) with lead oxide in a sealed tube (Dziewoński *et al.*, Ber. 1903, **36**, 962; 1914, **47**, 1679; 1918, **51**, 457), and purified by crystallisation from cumene or nitrobenzene. Forms large, glistening, golden-yellow needles, m.p. 387°, and gives a *picrate*, m.p. 295–296° (dec.).

Dziewoński and collaborators have shown by degradation with chromic acid and permanganate that decacyclene has the constitution :



(Ber. 1913, **46**, 2156).

It may be reduced by hydriodic acid and red phosphorus in a sealed tube (Dziewoński *et al.*, J.C.S. 1924, **126**, i, 1056) or catalytically using nickel at 230° and 200 atmospheres pressure (von Braun, Ber. 1934, **67**, [B], 214). Sulphonation yields a trisulphonic acid, the alkali salts of which dye wool various shades of red and violet from an acid bath (Dziewoński and Pochwalski, A, 1926, 279; G.P. 379616, U.S.P. 1496085).

Klarner and Woszczerowicz (Chem. Zentr. 1934, I, 1760) describe both absorption and fluorescence spectra.

DECAMETHYLENEDICARBOXYLIC ACID, $CO_2H\cdot[CH_2]_{10}\cdot CO_2H$. The ester is prepared by electrolysis of potassium ethyl pimelate in alkaline solution (G. Komppa, Ber. 1901, **34**, 900 ; J. Walker and J. Lumsden, J.C.S. 1901, **79**, 1200). It is also obtained by adding hydrobromic acid to undecylinic methylester and converting this to the nitrile ester with subsequent hydrolysis (Walker and Lumsden, *l.c.*, H. Noerdlinger, Ber. **1890**, **23**, 2357. For related methods, *see* J. von Braun, Ber. 1909, **42**, 4550; A. Franke and A. Kroupa, Monatsh. 1930, **56**, 331). A commercial process utilises di*cyclo*hexanol which is oxidised (chromic acid) to diketodecamethylene-ακ-dicarboxylic acid and this last is reduced by the Clemmensen method (G.P. 602837). Decamethylene-ακ-dicarboxylic acid has also been obtained by oxidising several natural products, *e.g.* behenolic acid (T. Maruyama, Proc. Imp. Acad. Tokyo, 1934, **10**, 467; the reverse synthesis has been effected by J. L. Simonsen and co-workers, J.C.S. 1928, 2678); *iso*oleic acid (K. H. Bauer and J. Mitsotakis, Chem. Umschau, 1928, **35**, 137); *iso*erucic acid (J. L. Simonsen and co-workers, J.C.S. 1927, 371); λ-hydroxy stearic acid (Y. Asahina and H. Takimoto, J. Pharm. Soc. Japan, 1929, **49**, 155); and by reduction of a decadiene acid contained in sardine oil (Y. Toyama and T. Tsuchiya, Bull. Chem. Soc. Japan, 1935, **10**, 192).

Decamethylene-$\alpha\kappa$-dicarboxylic acid has m.p. 125° (Maruyama), 126·5° (Franke and Kroupa), 129° (corr.) (D. A. Fairweather, Proc. Roy. Soc. Edin. 1925, **46**, 71). For X-ray measurements of the acid and esters, *see* A. Normand, J. Ross, and E. Henderson, *ibid.* 1926, **47**, 69; J.C.S. 1926, 2632.

The half-esters yield esters of eicosane-1:20-dicarboxylic acid on electrolysis (D. A. Fairweather, *l.c.*; L. Ruzicka and co-workers, Helv. Chim. Acta, 1928, **11**, 1174). *cyclo*-Undecanone and *cyclo*dokosane-1:12-dione are formed on distilling the rare earth salts (*e.g.* thorium and particularly yttrium) of the acid (B.P. 235540; L. Ruzicka and co-workers, Helv. Chim. Acta, 1926, **9**, 249; 1928, **11**, 670.

DECCAN GRASS CEREALS, Millett (Vol. II, p. 482*c*).

DECHENITE. Lead vanadite containing zinc and manganese.

DECHOLIN. Trade name for preparations containing dehydrocholic acid, employed in treating hepatic diseases (*Riedel- de Haen, Berlin; Old Strand Chemical and Drug Co., London*). B.P.C. 1934.

DECOLORISING CARBONS *v.* CHARCOAL, ACTIVATED.

DECYL ALCOHOL (and ACETATE). *n*-Decyl alcohol, $C_{10}H_{21}\cdot OH$, is used, but in very small amount, in perfumes of the rose, neroli, and orange type. Not more than 1% should be used in rose perfumes. Sp.gr. at 15·5° 0·836, n_D^{20} 1·4375, b.p. 232°. Decyl acetate, $C_{10}H_{21}\cdot OOC\cdot CH_3$, has a sweet, fruity odour, and is used to give a distinctive note to many floral perfumes. B.p. 190°.

E. J. P.

DECYL ALDEHYDE, n-$C_9H_{19}\cdot CHO$. This synthetic perfume is so powerful that it is usually sold in a 10% alcohol solution, and must be used in traces only. It has an intense, sweet odour, allied to that of orange, and is used—in traces—in floral compounds of the jasmin, rose, violet and wallflower types. When freshly made it melts at 18–20°; b.p. at 12 mm. 94°, at 760 mm. 210°; sp.gr. at 15·5° 0·828; n_D^{20} 1·4296.

E. J. P.

DEGALOL. *m*-Dihydroxycholic acid for the treatment of cholelithiasis. (*Riedel-de Haen; Old Strand Chemical and Drug Co.*) B.P.C. 1934.

DÉGRAS (MOËLLON) or SOD OIL is the waste fat recovered as a by-product from the chamoising (oil-tanning) process, and is used for the currying (stuffing) of heavy leathers and the fat-liquoring of light leathers; its value for these purposes is such that in some factories skins are chamoised solely for the sake of producing the moëllon. For the production of chamois leather, the flesh-splits of sheepskins are used, which are usually de-limed by "drenching." The wet skins (partially dried by "stocking" with sawdust) are stretched on tables and rubbed with fish oil—in England cod (liver)-oil is chiefly used, but whale oil and seal oil are also employed on the Continent, and menhaden oil in America—and then pummelled and worked in the "stocks" so as to become thoroughly impregnated with the oil. The skins are then hung in the air to cool, and the process of rubbing in the oil, stamping in the stocks and airing is repeated until enough oil has been adsorbed. By the exposure to the air, the oil undergoes partial oxidation and hydrolysis, which is accompanied by the evolution of volatile products, among which acrolein is noticeable in the later stages. In the so-called English or German methods of working, the oxidation is promoted by piling the skins together in boxes or in covered heaps (after, or between, the stockings) in order to retain the heat generated by the oxidation; the skins must be turned or cooled occasionally, however, in order to prevent overheating. In the French method the skins are "stocked," aired, and "fermented" under milder conditions than in the English method, so that the oil becomes less thickened, and it is possible to recover a large part of the surplus unadsorbed oil by steeping the leathers in warm water and wringing them, or pressing them in hydraulic presses: the fatty matter so expressed is termed *première torse moëllon* (*moëllon dégras* in the United States).[1] A further quantity of grease is recovered from the skins by washing them with hot solutions of soda or potash, as is done in the English or German methods; the inferior dégras obtained in this way is frequently added to the moëllon. In the classical English or German method of working, the oil becomes so thickened as a result of the more intense heating that it cannot be pressed out of the skins, and the whole must be recovered by washing with hot alkaline lyes; the emulsion so obtained is acidified with sulphuric acid, when the fatty matter separates and can be skimmed off. This product constitutes the *sod oil* of commerce. According to Proctor, however, many English manufacturers have now adopted a modified procedure, akin to the French method, and recover a considerable quantity of moëllon by pressure (Proctor, "Principles of Leather Manufacture," 2nd ed., 1922, p. 459); the same is the case in American practice (*cf.* J. A. Wilson, "Chemistry of Leather Manufacture," A.C.S. Monograph, 1929, vol. II, p. 719).

The mechanism of the changes that occur during chamoising is still very imperfectly understood. Evidently considerable oxidation and hydrolysis of the oil takes place, and part of the applied unsaturated oil enters into some form of irreversible combination with the skin substance, since only a limited portion of the oil adsorbed by the leather can be recovered by extraction with solvents: moreover, the skin undergoes a true tanning ("oil-tannage") since extraction with solvents does not restore it to the condition of pelt, as is the case if it is attempted to "chamoise" the skin with a saturated acid, *e.g.* stearic acid. Chambard and Michallet (J. Int. Soc. Leather Trades Chem. 1927, **11**, 559) regard the chamoising process as comprising two distinct reactions, *viz.* (1) the tanning proper, whereby the moist skin substance is converted into the more stable leather-substance by the action of the unsaturated oil with the participation of oxygen (*cf.* Lauffmann, Ledertech. Rundschau, 1926, **18**, 191), and (2) a secondary "stuffing" or nourishing action whereby relatively inert and polymerised derivatives of the oil are adsorbed by the leather fibrils. The first reaction may take the course suggested by Fahrion (Z. angew. Chem. 1891, **4**, 172, 634; 1903, **16**, 670; 1909, **22**, 2083; *cf.* Meunier and Seyewetz, Coll. 1908, 203; Chim. et Ind. 1918, (i), 79), *viz.* (i) a peroxidation of at least two of the unsaturated linkings of the polyethylenic fatty acid chain, followed by (ii) the combination (oxidation) of two protein (amino) groups of the skin-substance with one of the peroxide groups, whilst the hydrogen so liberated is absorbed at the second peroxidised linking to form a labile di-hydroxy group; the latter may pass finally into a more stable form, perhaps by lactonisation with the carboxyl group liberated by hydrolysis of the oil. Tautomeric change of the dihydroxy groups into the keto-hydroxy form, or the conversion of peroxide groups into monoxide (epoxide) groups and other subsidiary oxidation reactions may account for the formation of the inert "oxidised" acids or their glycerides which are found in the unadsorbed moëllon, and for the appearance of other oxidation products (aldehydes, volatile fatty acids, etc.) during the chamoising process. Fahrion's theory that the intermediate, labile oxidation derivatives (peroxides ?) of the oils or fatty acids are the actual tanning agents is supported by the fact that neither recovered dégras, nor "blown oils," nor the "oxidised acids" from these, possess appreciable chamoising power. The presence of moisture in the skin is essential in order to bring it to the condition of a permeable, reactive gel; it is probable, however, that the water also plays a chemical rôle—in the partial hydrolysis of the oils, for instance. True tanning (chamoising) can also be procured by means of linseed oil, but the resultant leather is inferior in suppleness and softness to a good chamois leather prepared by means of cod-liver oil; a harsh leather is also obtained when fish oil fatty acids are used in place of the glycerides (*cf.* Fahrion, G.P. 338476; Lewkowitsch and Wood, B.P. 13126, 1911), and the recovered dégras is unsatisfactory.

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[1] It may be noted that in the United States wool grease is commonly known as "dégras" or "sod oil," and must not be confused with the "moëllon dégras" obtained from cod-liver oil by chamoising. In Europe, also, the term "dégras" is indefinite, as it also embraces the mixed commercial stuffing greases and leather-greases obtained from tanned skins and clippings.

Moëllon possesses considerable emulsifying powers, and contains usually about 20–25% of water; the most characteristic constituents are the resinous "oxidised fatty acids" obtained upon saponification, and termed *dégras-former* (*dégragène, Dégrasbildner*) by Simand (Gerber, 1890, **16**, 243, 254, 266, 279); these are insoluble in light petroleum, but soluble in alcohol and alkaline solutions, from which they are precipitated by the addition of mineral acid; according to Fahrion, they consist of a complicated mixture of oxidised (peroxidised, hydroxylated ?) acids.

The characters of pure "moëllon-dégras" are illustrated by the figures in Table I (due to J. A. Wilson, *op. cit.*, p. 800; Wilson and Merrill, "Analysis of Leather," 1931, p. 383); *cf. also* Ruhsam, J.S.C.I. 1892, **11**, 639; Tortelli, Ann. d. Lab. chim. d. Gabelle, 1897, 184; Schmitz-Dumont, Dingl. Polyt. J. 1895, **296**, No. 9–11; (these, with other figures, are reproduced by Lewkowitsch in "Oils, Fats, and Waxes," vol. III (6th ed.), 1921, pp. 435–9).

Moëllon is not used in its pure state for currying, but is mixed with fish or blubber oils, tallow, etc., and sometimes wool grease, to form the ordinary commercial dégras; according to trade custom, such products are regarded as genuine. (Standards for *commercial* moëllon and dégras, issued by the German Verband der Dégras- u. Lederoelfabrikanten (*cf.* Gnamm, "Die Fettestoffe in der Lederindustrie," Stuttgart, 1926, p. 535) are shown in Table II.) On the other hand, numerous substitutes for dégras or *artificial dégras* occur in commerce, which consist of highly adulterated dégras, the

TABLE I.

ANALYSIS OF MOËLLON-DÉGRAS (WILSON).

	"Typical sample." %	Average figures. %
Free fatty acids (as oleic acid)	21·4	15·7
Unsaponifiable matter	1·2	1·7
Unoxidised fatty acids	49·7 (iod. val. 79; m.p. 33°C.)	51·9 (iod. val. 80; m.p. 28°C.)
Oxidised fatty acids .	12·8 (iod. val. 88)	10·4 (iod. val. 83)
Water	23·1	25·3
Ash	1·0	0·8
Free mineral acid . .	0	0

TABLE II.

GERMAN STANDARDS FOR COMMERCIAL MOËLLON AND DÉGRAS.

	"Moëllon."	"Moëllon-Dégras."	"Dégras."
	%	%	%
Total fatty matter [1] . .	80	78	75
Saponifiable matter [1] .	70	63	55
Unsaponifiable matter .	10	15	20
Oxidised acids . . .	6–8	5–7	4–6
Volatile matter (water) .	20	22	25
Ash	$\not>1$	$\not>1$	$\not>1$

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[1] A tolerance of 2% is permitted in these figures.

adulterants including mineral oils, blown oils, rosin, blown rosin oils, etc.; according to the German standards (*see above*) rosin is not tolerated in " moëllon " or " dégras," but may be accepted in products sold as " leather oils " provided its presence is declared.

For methods of analysis of dégras, *cf.* Lewkowitsch, " Oils, Fats, and Waxes," vol. III, Ch. 16 (2); Auerbach, Coll. 1931, 311; (provisionally adopted as official methods by the Int. Ver. Lederind.-Chem.); Immendörfer, Collegium 1925, 135; American standard methods—J. Amer. Leather Chem. Assoc. 1927, **22**, 567.

E. L.

DEGUELIN *v.* DERRIS.

DEHYDRASE, DEHYDROGENASE. The reducing enzymes are the most labile biocatalysts known. Their isolation from the tissues by methods analogous to those used for the hydrolysing enzymes is usually impossible; perhaps they are closely bound up with the structural elements of the cell. They are usually studied by Thunberg's (Skand. Archiv. 1920, **20**, 1) methylene blue technique, which consists essentially in determining the reduction time of the dyestuff in the presence of the cell and its substrate, the experiment being made in vacuum tubes under anaerobic conditions. The substances which reduce the dyestuff are known as hydrogen donators, the substances which can be reduced in presence of the cell are termed hydrogen acceptors and the catalysts as dehydrogenases.

Whilst many substances are active as donators in presence of the cell, many others, closely related in chemical structure, are inert. It is considered, in explanation of this selectivity of action, that there are relatively few dehydrogenases, but that each deals with a particular type of molecule rather than with a specific substrate (Quastel, Trans. Faraday Soc. 1930, **26**, 853). Quastel has emphasised that the essential happening is a change in the substrate molecule as a whole prior to reaction. This is spoken of as the activation of the molecule (Ergebnisse der Enzymforschung, 1932, **1**, 209).

Methods of preparing active dehydrogenases from tissues by crushing them very finely in a steel ball mill are described by Ogston and Green (Biochem. J. 1935, **29**, 1983, 2005).

The principal dehydrogenases distinguished act on succinic, malic, formic, citric and lactic acids, xanthine and alcohol.

Succinic dehydrogenase converts succinic acid into fumaric acid in presence of methylene blue. It is present in bacteria and in muscle tissue (Thunberg, Skand. Arch. Physiol. 1917, **35**, 165; Wieland and Frage, Annalen, 1929, **477**, 1). It has a high specificity.

The so-called Schardinger enzyme of milk converts aldehyde to acid, hypoxanthin and xanthin to uric acid (Wieland, Ber. 1914, **47**, 2085; Annalen, 1929, **477**, 32; 1930, **483**, 217).

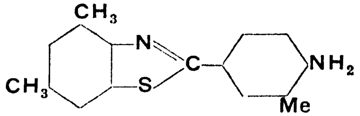
The dehydrase of the acetic bacteria converts alcohol into aldehyde and this into acid, the oxygen acting as acceptor in presence of the enzyme. An alternative theory is that a second molecule of aldehyde acts as acceptor for the first (Wieland, Ber. 1913, **46**, 3327; Wieland and Bertho, Annalen, 1928, **467**, 95; 1929, **474**, 1; Bertho and Baso, Annalen, 1931, **485**, 26; also summary by Bertho, Ergebnisse der Enzymforschung, 1933, **2**, 204). The acceptor used for studying these reactions is quinone.

Citric acid dehydrase is present in the liver and in vegetable material acting on citric acid (Bernheim, Biochem. J. 1928, **22**, 1178; Thunberg, Amer. J. Physiol. 1931, **90**, 540).

The dehydrases of seeds have been studied by Fodor (Biochem. Z. 1930, **225**, 409, 417; 1932, **246**, 4). The subject is too involved for further treatment here; reference is made to the most recent summary articles by Quastel and by Bertho in Ergebnisse der Enzymforschung, 1933, **1**, 209; 1934, **2**, 204.

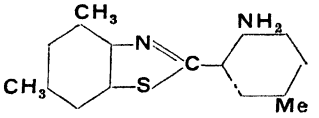
E. F. A.

DEHYDROTHIO-*m*-XYLIDINE,



is prepared together with about an equal amount of *isodehydrothio-*m*-xylidine* when *m*-xylidine is heated with sulphur. The excess of *m*-xylidine is removed by distillation and the residue treated with hydrochloric acid in which the *iso*-compound is insoluble. Dehydrothio-*m*-xylidine has m.p. 107°, b.p. 283°/14 mm., is insoluble in water, readily soluble in hot alcohol (Anschütz and Schultz, Ber. 1889, **22**, 582; Paul, Z. angew. Chem. 1896, **9**, 679), and may be sulphonated (G.P. 593632).

Both dehydrothio-*m*-xylidine and the ***iso*-**compound yield azo-dyes, but only those from the latter are substantive to cotton. ***iso*-**Dehydrothio-*m*-xylidine, m.p. 121°, has been shown to have the structure:



(Anschütz and Schultz, Ber. 1925, **8**, [B], 64).

DEKOL. Sulphite cellulose waste liquor used as a wetting-out agent.

DEKRYSIL. Trade name for 4:6-dinitro-*o*-cresol, used in the treatment of obesity (*British Colloids, London*). B.P.C. 1934.

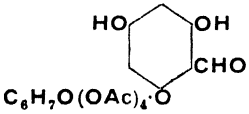
DELATYNITE *v.* AMBER OR SUCCINITE.

DELCOSINE *v.* DELPHINIUM SPECIES, ALKALOIDS OF.

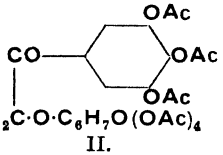
DELPHIN is the 3:5-diglucoside of delphinidin (*q.v.*). Qualitative tests (Robinson and Robinson, Biochem. J. 1931, **25**, 1687) had already indicated the possibly wide occurrence of an anthocyanin of this type when Reynolds, Robinson and Scott-Moncrieff (J.C.S. 1934, 1235) succeeded in isolating delphin from the bright blue flowers of *Salvia patens.* The pigment, which is present as a complex acyl derivative, is accompanied by a large proportion of anthoxanthins. The latter remain in solution when aqueous lead acetate is added gradually to a solution of the mixture in methyl alcoholic HCl, the anthocyanin being precipitated as a lead salt. Hydrolysis of acyl groups occurs when the regenerated anthocyanin is kept in contact with aqueous-alcoholic HCl, and recrystallisation of the simplified pigment gives delphin chloride. The pure diglucoside separates from 3% HCl in homogeneous, flat, leaf-like crystals having a striking bronze reflex, and when dried in air consist of a *trihydrate*,

$$C_{27}H_{31}O_{17}Cl,3H_2O.$$

The *chloride* is very sparingly soluble in cold water, alcohol and dilute acids, but it dissolves readily in hot dilute HCl. The *pseudo-base* is formed when the chloride is heated with water or alcohol. The solution in aqueous sodium carbonate is bright pure blue fading slowly to clear green. Sodium acetate gives a violet-blue, and ferric chloride added to the aqueous solution develops a bluish-violet coloration. In alcoholic solution the iron reaction is violet blue. A royal blue precipitate is formed when lead acetate is added to a solution of the chloride. Boiling 10% HCl hydrolyses the anthocyanin to delphinidin chloride (1 mol.) and glucose (2 mols.). Careful comparison of the colour reactions of delphin with those of synthetic anthocyanins of known constitution enabled Reynolds, Robinson and Scott-Moncrieff (*l.c.*). to relate delphin to cyanin (*q.v.*), that is, to assign to delphin the constitution of a 3:5-diglucoside of delphinidin. Delphin chloride was synthesised by condensing together in ice-cold ethyl acetate solution saturated with dry HCl 2-O-tetra-acetyl-β-glucosidylphloroglucinaldehyde (I) and ω-tetra-acetyl-β-glucosidoxy-3:4:5-triacetoxy-acetophenone (II). An acetylated anthocyanin resulted from which delphin chloride (III) was obtained after hydrolysis with methyl alcoholic barium hydroxide and treatment with dilute sulphuric and hydrochloric acids.



I.



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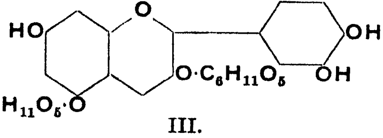


III.

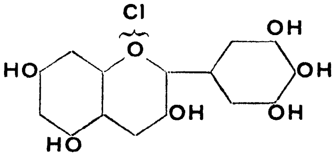
Both the natural and synthetic anthocyanin have identical quantitative colour reactions, absorption spectra in 0·1% methyl alcoholic HCl, and distribution ratios between 0·5% HCl and *n*-butyl alcohol. A saturated solution of the natural anthocyanin in 1% methyl alcoholic HCl is incapable of dissolving even traces of the synthetic salt, and *vice versa*; on the other hand, the chlorides of malvin, cyanin and mecocyanin dissolve in the mixed natural and synthetic delphin solutions.

Awobanin, the colouring matter of the flowers of *Commelina communis* var. *hortensis* Making is a derivative of delphin. Both the *chloride* and the *picrate* crystallise with $5H_2O$. The results of analysis and hydrolysis indicate that it is an ester derived from delphin (1 mol.) and *p*-coumaric acid (1 mol.) (Chika Kuroda, Bull. Chem. Soc. Japan, 1936, **11**, 265).

W. B.

DELPHINIDIN, first obtained by Willstätter and Mieg (Annalen, 1915, **408**, 61) by hydrolysis of delphinin (*q.v.*), has since been recognised as one of the most widely distributed anthocyanidins. An acylated monoglucoside, *Gentianin*, occurs in the flowers of *Gentiana acaulis*; an acylated rhamnoglucoside, *Violanin*, is present in the flowers of the violet pansy (*Viola tricolor* L.). *Vicin*, the colouring matter of the scarlet-red vetch (*Vicia* L.), is a mixture of a monoglucoside and a monorhamnoside of delphinidin. The egg-plant (*Solanum Melongena* L., var. *esculentum* Ness) owes its colour to *Nasunin*, a 3-bioside of delphinidin. A dimethyl ether, *Malvidin*, is a component of many anthocyanins amongst which are *Malvin*, *Oenin* (syn. *Ampelopsin*, *Cyclamin*), *Primulin*, and *Negretein*. A trimethyl ether, *Hirsutidin*, occurs in the diglucoside *Hirsutin*, and *Petunin* may be the corresponding diglucoside of a delphinidin monomethyl ether (Bell and Robinson, J.C.S. 1934, 1604).

Delphinidin chloride, $C_{15}H_{11}O_7Cl$,



may be obtained by hydrolysing any of the related glycosides by short boiling with 20% HCl, or synthetically as described below. Willstätter and Weil (Annalen, 1916, **412**, 178) have described four distinct hydrates having $1H_2O$, $1·5H_2O$, $2H_2O$, and $4H_2O$ respectively, whilst Reynolds, Robinson and Scott-Moncrieff (J.C.S. 1934, 1239) have encountered a fifth form with $3·5H_2O$. The *monohydrate* separates from cold 3–5% HCl as thin, sharply-cut, deep-violet rhombic tablets. The *sesquihydrate* crystallises from HCl of more than 20% concentration. It is readily obtained by adding concentrated HCl to a solution of delphinidin in water or dilute HCl; an amorphous precipitate is first formed but this soon crystallises. The *dihydrate* is obtained when the solvent is allowed to evaporate slowly from a solution of delphinidin in alcohol to which 7–20% HCl has been added; it forms aggregates of prismatic tablets. The *tetrahydrate* separates from solution in 5% HCl in the form of fine red-brown prisms and needles. Of the various forms the *sesqui-* and *tetra*-hydrates are most easily prepared. Robinson's *hydrate* was obtained by dissolving delphinidin chloride in 0·5% HCl and increasing the acid concentration to 10%. The *chloride* is easily soluble in methyl or ethyl alcohol and in water to violet solutions; it dissolves with difficulty in dilute sulphuric acid. Sodium carbonate added to a solution of the chloride gives a pure blue coloration. With ferric chloride the alcoholic solution gives a pure blue, whilst in aqueous solution the colour is violet and less stable. The absorption spectrum consists of one fairly well defined band in the yellow-green region. The anhydrous chloride does not melt below 350°. The *sulphate* separates from hot dilute sulphuric acid in long prisms. The *picrate* forms fine red-brown needles and prisms difficultly soluble in water. The *iodide* is of particular interest, since it is easily obtained crystalline even when it is derived from crude specimens of delphinidin. It separates when concentrated HI is added to a solution of the chloride in dilute HCl and crystallises from hot dilute HI in elongated rhombic plates which are frequently arranged in rosettes. The crystals are deep-red by transmitted light and exhibit a marked yellow glitter. An aqueous solution of the chloride soon deposits violet flocks of the *colour-base*. The *pseudo-base*, $C_{15}H_{12}O_8$, is formed when a dilute solution of the chloride is warmed with a trace of sodium dihydrogen phosphate. It has considerable crystallising power; extracted with ether and recrystallised from ether or water it forms colourless prisms which become violet when heated above 120°. It is easily soluble in alcohol, acetone, ethyl acetate or glacial acetic acid, but is less soluble in ether and insoluble in benzene. It dissolves in aqueous sodium carbonate to a yellow solution. Dilute HCl regenerates the chloride.

Delphinidin chloride dyes unmordanted wool violet. On tin-mordanted wool the dyeing is blue with a violet tinge. Tannined cotton is dyed blue-violet.

An indication of the constitution of delphinidin was obtained by Willstätter and Mieg (*l.c.*), who considered that phloroglucinol, pyrogallol, and a small amount of gallic acid were the products obtained on hydrolysing delphinidin chloride with 75% KOH at 250°. Complete proof of structure was provided by Pratt and Robinson (J.C.S. 1925, **127**, 173), who condensed ω-3:4:5-tetramethoxyacetophenone with 2-hydroxy-4:6-dimethoxybenzaldehyde in ether saturated with dry hydrogen chloride, and obtained delphinidin chloride hexamethyl ether. Demethylation with HI (sp.gr. 1·7) and phenol gave delphinidin iodide, from which the chloride, identical in all respects with that obtained from natural sources, was obtained by warming in alcoholic solution with silver chloride. A more convenient method of preparing delphinidin consists in condensing 2-O-benzoylphloroglucinaldehyde with ω-3:4:5-tetra-acetoxyacetophenone to benzoyldelphinidin chloride, from which delphinidin is obtained by successive treatments in an inert atmosphere with aqueous KOH and HCl (Bradley, Robinson, and Schwarzenbach, J.C.S. 1930, 793).

Delphinidin chloride may be distinguished from other anthocyanidins in that it is not extracted from 1% hydrochloric acid solution by the so-called "delphinidin reagent." This consists of anisole (4 vols.) and ethyl amyl ether (1 vol.) containing 5 g. picric acid in 100 c.c. of the mixed solvents. Aerated dilute acid solutions of both delphinidin and petunidin are immediately decolorised as the result of oxidation when they are mixed with excess of 10% aqueous sodium hydroxide (R. Robinson).

W. B.

DELPHININ, the pigment of the purple wild delphinium (*Delphinium Consolida* Linn.), was isolated by Willstätter and Mieg (Annalen, 1915, **408**, 61). It is an ester of a delphinidin diglucoside (1 mol.) and *p*-hydroxybenzoic acid (2 mols.), the acyl residues being attached to phenolic hydroxyl groups (Kondo, Helv. Chim. Acta, 1928, **11**, 919). Delphinin is best isolated as the *chloride*, $C_{41}H_{39}O_{21}Cl$, which appears to crystallise with $12H_2O$, of which only $10H_2O$ can be removed by drying in high vacuum at 130°. It forms deep red prismatic tablets or prisms, and dried as above sinters at 150–160°, then melts at 200–203° with decomposition and swelling. Although easily soluble in methyl alcohol, it dissolves with difficulty in ethyl alcohol, in HCl of more than 0·5% concentration and in dilute sulphuric acid. The solution in sodium carbonate is blue, and ferric chloride added to an aqueous or alcoholic solution gives a blue colour. The salt is optically active; $[\alpha]_C = -1364°(\pm 150°)$; $[\alpha]_{614} = -2273°$ $(\pm 150°)$. Its absorption spectrum consists of one broad band. When the neutral aqueous solution is allowed to stand the *colour base* (rosettes of violet needles from aqueous alcohol) is formed; *pseudo-base* formation is not observed even when the chloride is warmed with water. The *picrate*, obtained as a flocculent red-brown precipitate, is very difficultly soluble in water.

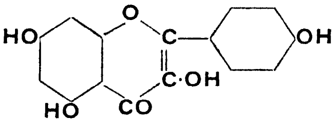
W. B.

DELPHININE *v.* DELPHINIUM SPECIES, ALKALOIDS OF.

DELPHINIUM CONSOLIDA. *Delphinium Consolida* is a common European plant belonging to the larkspur family; its name refers to its powers, real or imaginary, of healing or consolidating wounds. The blue flowers were examined by Perkin and Wilkinson (J.C.S. 1902, **81**, 585) to determine if these yield the same colouring matters as those previously isolated from the flowers of the *D. zalil* (*ibid.* 1898, **73**, 267). The presence of kaempferol only, however, could be detected. For its isolation an aqueous extract of the flowers was digested at the boil with addition of sulphuric acid, and the brown resinous product which separated on keeping, extracted with alcohol, and the extract concentrated. Addition of ether to this solution caused the precipitation of resinous impurity, and on evaporating the ethereal liquid a semi-crystalline residue of the crude colouring matter was obtained. The product was converted into the acetyl derivative, and this, after purification, retransformed into colouring matter. The yield was approximately 1%.

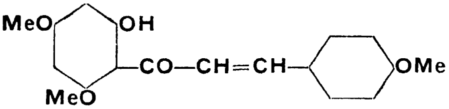
Kaempferol, $C_{15}H_{10}O_6$, yellow needles, m.p. 276–277°, is soluble in alkaline solutions with a yellow colour, and forms crystalline oxonium salts with mineral acids. When fused with alkali, it yields phloroglucinol and *p*-hydroxybenzoic acid.

To kaempferol v. Kostanecki (Ber. 1901, **34**, 3723) assigned the formula (I), and its synthesis



I.

was subsequently effected by v. Kostanecki, Lampe and Tambor (*ibid.* 1904, **37**, 2096) from 2-hydroxy-4:6:4′-trimethoxychalkone (II) by the usual method of flavonol synthesis. The *kaempferol* 5:7:4′-*trimethyl ether*, pale yellow needles, m.p. 151–152°, thus obtained yielded kaempferol (I) on demethylation.



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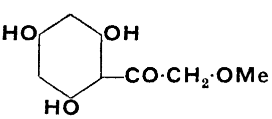

III.

Robinson and Shinoda (J.C.S. 1925, **127**, 1973) synthesised kaempferol by heating ω-methoxyphloracetophenone (III) with anisic anhydride and sodium anisate. The product, on hydrolysis, yielded *kaempferol* 3:4′-*dimethyl ether*, pale yellow platelets, m.p. 234°, from which kaempferol was obtained by demethylation.

Tetraacetylkaempferol, when crystallised from methyl alcohol, forms colourless needles, and when heated commences to melt at 116° and becomes completely fluid at 120°. On further heating, however, gradual solidification ensues and the product subsequently melts at 181–182°. This peculiarity of acetylkaempferol, which is not apparent when the substance is crystallised from ethyl alcohol, affords a convenient method for its detection.

Kaempferol possesses well-defined dyeing properties, and gives with mordanted woollen cloth the following shades which closely resemble those given by morin:

Chromium	*Aluminium*	*Tin*	*Iron*
Brownish-yellow	Yellow	Lemon-yellow	Deep olive-brown

Kaempferol is also present in the *Impatiens Balsamina* (Chantili Pass), the *Erythrina stricta* (vernacular name " Kon kathet ") (Perkin and Shulman, Proc. Chem. Soc. 1914, **30**, 177), the berries of the *Rhamnus catharticus*, and together with quercetin, both apparently as glucosides, in the flowers of the *Prunus spinosa* (Perkin and Phipps, J.C.S. 1904, **85**, 56).

Kaempferide (kaempferol 4′-methyl ether) exists in galanga root (*q.v.*).

The following glucosides of kaempferol are known: *Robinin*, which occurs in the flowers of *Robinia Pseudo-Acacia* (q.v.); *kaempferitrin*, found in the leaves of the *Indigofera arrecta* (*see* INDIGO, NATURAL); *kaempferin*, which has been isolated from *Cassia angustifolia*, Vahl. (Tutin, J.C.S. 1913, **103**, 2006); *multiflorin*, present in *Rosa multiflora* (Konda *et al.*, J. Pharm. Soc. Japan, 1929, **49**, 35, 182); and a *kaempferol rhamnoside* which exists in the blossoms of *Acacia discolor*, *A. linifolia*, *A. decurrens* (var. *mollis*), and *A. longifolia* (Petrie, Biochem. J. 1924, **18**, 957).

Willstätter and Mieg (Annalen, 1915, **408**, 61) isolated from the flowers of *D. Consolida* the anthocyanin, *delphinin* (*q.v.*).

A. G. P. and E. J. C.

DELPHINIUM SPECIES, ALKALOIDS OF. *Larkspur*, *pied d'alouette*, *dauphin* (Fr.), *Rittersporn* (Ger.). Fam. Ranunculaceæ. About 12 delphinium species are known to contain alkaloids, but only the constituents of *D. Ajacis*, *D. Consolida*, and *D. Staphisagria* have been studied to some extent. Heyl (J.C.S. 1903, **84**, I, 650) isolated a mixture of bases which he called *delphocurarine* from the roots of *D. bicolor* (0·27%), *D. Menziesii* (0·35%), *D. Nelsonii* (0·72%), and *D. scopulorum* var. *stachyd.* (1·3%). The bases were extracted by 80% alcohol containing tartaric acid. The white amorphous mixture exerted a strong curare-like action (*cf.* Lohmann, Pflüger's Archiv. 1902, **92**, 398). From the mixture, a small fraction of a crystalline base, $C_{23}H_{33}O_7N$ (?), was isolated, m.p. 184–185° (from ether and light petroleum), soluble in EtOH, Et_2O, $CHCl_3$, benzene, sparingly soluble in light petroleum ; it contains 18·03% OMe, but does not give crystalline salts or characteristic colour reactions.

Uncharacterised alkaloids are recorded from *D. glaucum*, *D. Geyeri* (Heyl, Hepner and Loy, J. Amer. Chem. Soc. 1913, **35**, 880), and *D. Andersonii* Gray (Miller, Amer. Chem. Abstr. 1923, **17**, 3073). According to Keller (Arch. Pharm. 1925, **263**, 275), *D. elatum* contains an alkaloid, $C_{33}H_{51}NO_8$ (0·35%), melting at 218°, the oily mother liquor is said to contain two more alkaloids, but no further details have been reported.

D. Ajacis contains alkaloids of a considerably smaller molecular weight, from an alcoholic extract of the seeds Keller and Völker (Arch. Pharm. 1913, **251**, 207) succeeded in isolating two new bases.

Ajacine, $C_{15}H_{21}NO_4+H_2O$, separates from dilute EtOH, m.p. 142–143°, soluble in MeOH, EtOH, $CHCl_3$, benzene, ligroin, acetone, sparingly soluble in Et_2O and $CH_3{\cdot}CO_2Et$, insoluble in H_2O. It is alkaline in reaction, yields readily soluble salts, which crystallise with difficulty (hydrochloride, sulphate). The base contains three OMe groups.

Ajaconin, $C_{17}H_{29}NO_2$, crystallises in prisms, m.p. 162°–163°, is probably a secondary base, does not contain methoxyl-groups, yields a crystalline methiodide, m.p. 121°, and an amorphous di-benzoate.

D. consolida: (common larkspur, *Feldrittersporn*, Ger.). Keller (Arch. Pharm. 1910, **248**, 468) isolated three alkaloids from this plant (crude hydrochlorides 1%), one being crystalline, m.p. 195–197°, soluble in EtOH, $CHCl_3$, acetone, MeOH, sparingly soluble in Et_2O and $CH_3{\cdot}CO_2Et$, insoluble in H_2O, strongly alkaline. Markwood (Amer. Chem. Abstr. 1925, **19**, 874) re-investigated *D. consolida* and isolated two crystalline alkaloids, **delsoline**, $C_{25}H_{41}NO_8$, m.p. 207–209°, soluble in EtOH and $CHCl_3$, and **delcosine**, $C_{21}H_{33}NO_6$, m.p. 198–199°, soluble in EtOH and $CHCl_3$, sparingly soluble in Et_2O, the latter being probably identical with Keller's crystalline base (*see above*).

D. Staphisagria: (stavesacre-seeds, *Stephanskraut*, *Läusekraut*, Ger.). For early literature, *cf.* Walz (Arch. Pharm. 1922, **260**, 9). The most important alkaloid is **delphinine**, $C_{34}H_{47}NO_9$, m.p. 187·5–188·5°, $[\alpha]_D^{20}$ +18·9°, crystallises from Et_2O or acetone, soluble in the usual organic solvents. The acid oxalate is characteristic, it crystallises in needles, m.p. 186° (dried). Delphinine is a tertiary base (methiodide, m.p. 196°) it contains one free hydroxyl, one benzoyl, and four methoxylgroups. Delphinine, like most of the *D.*-alkaloids, is apparently structurally related to aconitine. Keller and Schmechel (Arch. Pharm. 1925, **263**, 276) give a detailed account of the extraction of staphisagria-seeds (yield 0·16% total alkaloids) from which 0·11% crystallised delphinine, small amounts of **delphisine**, a third crystalline base and amorphous bases were obtained (**delphinoidine** and **staphisagroine** (?)). Keller and Schmechel (Arch. Pharm. 1925, **263**, 280) further investigated the constitution of delphinine, but so far no definite results have been published. For details concerning the essential oil of *D. Staphisagria*, *cf.* Markwood (Amer. Chem. Abstr. 1928, **22**, 1215).

Pharmacological Action of Delphinium Alkaloids.—*Delphinine* is intensely poisonous, resembling aconitine in its action and affecting especially the respiration and circulation by paralysing the nerves of the respiratory system. Lethal dose for dogs per kg. body-weight: *delphinine*, 1·5 mg., *delphisine* 0·7 mg., and *delphinoidine* 0·5 mg. For further details, *cf.* Lohmann (*l.c.*), Kahn (Pflüger's Archiv. 1916, **164**, 428), and Führer (Arch. exp. Path. Pharm. 1911, **66**, 187).

Schl.

DELPHINOIDINE *v.* Delphinium Species, Alkaloids of.

DELPHISINE *v.* Delphinium Species, Alkaloids of.

DELSOLINE *v.* Delphinium Species, Alkaloids of.

DELTA ACID, *a*-naphthylamine-4:8-disulphonic acid, is a valuable intermediate for the production of 1:8-dihydroxynaphthalene-4-sulphonic acid, of 5-sulpho-8-amino-*a*-naphthol, and of *a*-naphthol-4:8-disulphonic acid. It yields a blue wool dyestuff on fusing with sodium sulphide and hydroxide at 210° (G.P. 283727), but is more extensively used in the production of azo-dyestuffs directly (G.P. 43125) and of tetrakisazo-dyestuffs (F.P. 556489). It has also been employed in the preparation of light-sensitive paper which is coated with delta acid and a diazo-component, the red image being developed with alkali.

DENATURANTS. Various articles primarily used for human consumption, such as tea, tobacco, and spirits, are, on importation or manufacture in this country, subject to heavy Customs and Excise duties. When required for other purposes, for example, as raw materials in various arts or manufactures, they are released without payment of duty after having been denatured. This "denaturing" is accomplished by admixture with other substances which, while not impairing their efficiency for the purpose for which they are required, render them unfit for human consumption or act as "tell-tales" should they be deposited with the Government and "drawback" of duty claimed.

The principles underlying the choice of suitable denaturants are mainly as follows:

(*a*) They should be inexpensive so as not to add materially to the cost of the denatured article.

(*b*) Their use should cause the minimum amount of inconvenience to the manufacturer both in regard to his processes and to the necessary official supervision involved.

(*c*) The denaturant should not be incompatible with the process of manufacture or the subsequent use of the denatured article.

(*d*) If added for its nauseating effect it should be sufficiently objectionable to deter any would-be consumers of the denatured article.

(*e*) If added as a tell-tale it should be distinguishable easily by the microscope or other means.

(*f*) It should have such a relation to the original article as to preclude its removal from the mixture by any process which could profitably be carried out on a commercial scale, and it should be capable of being detected even if present in very small quantity.

The over-ruling condition in the use of denaturants is that they shall be approved by the Commissioners of Customs and Excise before use.

Spirit.—By reason of the large amount of revenue derived from alcoholic spirit and the great variety and extent of its commercial application this is the most important article subject to British official denaturing regulations. There are now in Great Britain four standard types of denatured alcohol, *viz.*:

Industrial Methylated Spirit.
Industrial Methylated Spirit (pyridinised).
Mineralised Methylated Spirit.
Power Methylated Spirit.

The quantity of methylated spirit manufactured in Great Britain and Northern Ireland during the past few years has steadily increased. The following table shows the quantity of spirit (expressed in proof gallons) received for methylation:

1931–2 . . .	10,497,268
1932–3 . . .	11,221,933
1933–4 . . .	12,961,041
1934–5 . . .	15,416,568
1935–6 . . .	16,303,078
1936–7 . . .	20,536,112

Industrial methylated spirit, which represents about 75% of the above quotation, consists of 95 parts by volume of alcohol and 5 parts of wood naphtha (in all methylating operations the Commissioners of Customs and Excise now have power to approve the use of synthetic "wood naphtha" in place of the wood distillation product hitherto used exclusively). Industrial methylated spirit (pyridinised) has the same composition as industrial methylated spirit with the addition of 0·5 parts of crude pyridine. Mineralised methylated spirit contains 90 parts by volume of alcohol, 9·5 parts of wood naphtha, and 0·5 of crude pyridine. To every 100 gallons of this mixture is added $\frac{3}{8}$ gallon of mineral naphtha (petroleum oil) and not less than $\frac{1}{40}$ oz. by weight of powdered methyl violet. Power methylated spirit is prepared by mixing 100 parts by volume of alcohol, not less than 5 parts of petrol or benzol, 0·5 parts of crude pyridine, and 2·5 parts of wood naphtha. To every 100 gallons of this mixture $\frac{1}{40}$ oz. of Spirit Red III dye must be added. When this preparation is mixed with not less than 25% of petrol, benzol or other approved substance, it may be sold free of further revenue restriction. The Statutory Regulations enable the Commissioners of Customs and Excise to permit variations from this prescribed formula. It might be mentioned that mineralised methylated spirit, in quantities not exceeding 4 gallons, and the fully denatured power methylated spirit can be sold by retail. With these exceptions a purchaser must have an Excise permit to cover the receipt of these forms of denatured alcohol.

The quantity of spirit used in the manufacture of power methylated spirit is rapidly increasing, as shown by the following table:

Year.	Proof gallons.
1931–2	32,103
1932–3	139,264
1933–4	604,527
1934–5	1,775,519
1935–6	1,556,627
1936–7	5,127,980

The general principles governing the denaturation of alcohol in the Dominions and foreign countries are the same as in Great Britain, variation being made to suit local requirements (*v.* ALCOHOL).

Tea.—Before being admitted into the United Kingdom, tea is examined by the Customs authorities under Sect. 30 of the Sale of Food and Drugs Act, 1875, and, if found satisfactory, it is passed on payment of duty; otherwise it is refused admission as tea for human consumption. It still, however, possesses a certain commercial value as a raw product for the extraction of theine or caffeine. If it is to be used for this or any other purpose except as a beverage the Commissioners of Customs and Excise permit its removal from bond without payment of duty on condition that it is suitably denatured. This is usually accomplished by the addition of 100 parts of lime and one of asafœtida to 1,000 parts of tea. Under special circumstances the asafœtida may, by permission of the Commissioners, be replaced by naphthalene or the lime may be replaced by an additional quantity of asafœtida.

Tobacco is almost entirely imported into this country in an unmanufactured condition. The process of manufacture results in the accumulation of considerable quantities of waste material (stalks, midrib and broken leaf). On these the duty which has been paid is returned as "drawback" to the manufacturer on condition either that the tobacco offal is surrendered to the Government or (if intended for such purposes as the manufacture of nicotine, insecticides, sheep dips, etc.) that it is denatured according to certain prescribed formulæ and under the supervision of revenue officers. Denaturing is equally necessary in the case of offal from tobacco manufactured in bond (although no duty has been paid nor drawback given) in order to prevent its fraudulent use as a substitute for tobacco on which duty has been paid. A standard formula for denaturing tobacco to be used in the manufacture of fumigants for horticultural purposes is:

Ground tobacco or offal snuff	92·5 parts.
Ground moss litter	7·5 ,,
Bone oil	2·5 ,,

For certain purposes anthracene oil, in the proportion of 10 parts, is used as an alternative for the bone oil. In these mixtures the oil acts as a deterrent to the use of the preparation as a smoking substitute for tobacco. The moss litter is a "tell-tale" to prevent the mixture, after removal of the oil and admixture with other offal snuff, from being fraudulently presented to the Government for drawback. Under certain circumstances the Commissioners of Customs and Excise are prepared to consider applications for permission to use ingredients supplementary to those prescribed above.

Wine which has become unsound and sour (owing to the formation of acetic acid), and thus unsuitable for use as a beverage, is released from Revenue custody without payment of duty, with a view to conversion into wine vinegar. The denaturant used in this case is 20% of commercial vinegar or an equivalent quantity of acetic acid.

F. G. H. T.

DENDRITES *v.* AGATE.

DENSIMETER. Apparatus for determining the sp.gr. of liquids.

DEOXYCARMINIC ACID *v.* COCHINEAL.

DEOXYSANTALIN *v.* BARWOOD.

DEPHLEGMATOR. A device for effecting fractional condensation in distillation practice thereby separating higher boiling constituents from mixed vapours (K. Thormann, "Destillieren und Rektifizieren," Leipzig, 1928).

DERBY RED *v.* AUSTRIAN CINNABAR.

DERICINEOL *v.* CASTOR OIL.

DERMATOL, bismuth subgallate, is employed as a drug, as a dusting powder (G.P. 381292), and in combination with quinine as "Etoscol" (Pharm. Ztg. 1925, **70**, 675). For review of manufacture, *see* E. A. Mauersberger (Chem. Weekblad, 1930, **27**, 337). The salt is recommended as a means of determining gallic acid (M. Hirsch, Chem. Ztg. 1927, **51**, 718) (*v.* BISMUTH, Vol. I, p. 700.

DERMOGENE. Trade name for an antiseptic dusting powder containing 55% of zinc peroxide.

DERMOL. Bismuth chrysophanate,

$$Bi(C_{15}H_9O_4)_3Bi_2O_3\ (?)$$

a yellow amorphous insoluble powder used in the treatment of skin diseases (*v.* Bismuth, Compounds of, and Chrysarobin).

DERRIS. Derris root has achieved its great importance in Europe and America as an insecticide and rival of pyrethrum since about 1919, prior to which it was known as the source of a fish poison obtained from many species and used by natives throughout the tropics. Although apparently 40 species are known to contain toxic constituents, *Derris elliptica*, *D. malaccensis*, and a so-called Sumatra type are the only ones of economic value. Derris root and its extracts (1) are cheaper and more potent than pyrethrum, and different crops are more constant and lasting in action; (2) they are simple and convenient to apply; (3) unlike lead and arsenic preparations which they replace, they are non-poisonous towards higher animals.

The preparation of active extracts consists in extracting with cold or warm water (10 and 16% extracts respectively), with 10% aqueous sodium bisulphite (such extracts are relatively more potent), or best with organic solvents, many industrial processes being based on such extractions. Thus extracts in alcohol or acetone yield stable colloidal solutions on diluting with water; the aqueous emulsion may be concentrated and either precipitated with milk of lime and the solid filtered and decomposed with tartaric acid, or treated with soda and the solid salted out. Powders so obtained have been applied directly, *e.g.* to tobacco plants, but are more frequently combined with sulphur, soap etc., in the preparation of spraying liquids and cattle washes (B.P. 214822). Other processes merely filter the extract, preferably after adding alcohol and concentrating (such a product contains 30–32% of *rotenone* and 34–35% of other toxic products) (B.P. 247140) or coagulate with metal salts before re-emulsifying with soaps (B.P. 226250) or sulphonated oils (B.P. 229773). Methyl alcohol, ether, chloroform, carbon tetrachloride and petroleum are among other solvents which have been suggested for the initial extraction (B.P. 239483). Still other processes employ a conventional protective colloid (gum arabic) to emulsify in water the toxic principles (H. A. Jones and W. M. Davidson, J. Econ. Entomol. 1931, 244) or their solution in higher alcohols (B.P. 285797).

The extraordinary activity of derris preparations is evidenced by the fact that fish are destroyed within 90–240 minutes in a 0·001% aqueous extract (W. Peyer and H. Hünerbein, Apoth.-Ztg. 1931, **92**, 1485). Rotenone, the chief toxic constituent, is equivalent at a dilution of 1 : 100,000 in water to nicotine at 1 : 10,000 and to pyrethrin at 1: 74,800 (M. Darley, J. Econ. Entomol. 1931, 111).

The predominating insecticidal constituents of derris root are *rotenone*, *deguelin*, *tephrosin*, and *toxicarol*, of relative toxicities 400 : 40 : 10 : 1 (Davidson *ibid.* 1930, 868). *See* Derris Resin.

DERRIS RESIN. Derris "root" is the dried rhizome of *Derris elliptica*, *D. malaccensis*, and other species. It is indigenous to Malaya and the East Indies. The resin is extracted from the roots by various organic solvents. It has come into considerable use as an insecticide, and has recently received a great deal of attention from investigators. Its principal toxic constituent is a crystalline body termed rotenone, first isolated by Nagai (J. Tokyo Chem. Soc. 1902, **23**, 740). The uncrystallisable portion of the resin, however, is probably as, or nearly as, toxic as the rotenone. Clark heated the uncrystallisable portion with alkali and isolated bodies to which the names toxicarol, deguelin, and tephrosin were given (J. Amer. Chem. Soc. 1930, **52**, 2461 ; 1931, **53**, 313, 759 ; 1932, **54**, 2537). These bodies are probably decomposition products of the uncrystallisable resin. Haller and La Forge (*ibid.* 1934, **56**, 2415) obtained dihydrodeguelin by reduction of a fraction of the resin. Cahn and Boam (J.S.C.I. 1935, **54**, 42T) have isolated a new substance from what was probably the extract from the root of *Derris malaccensis*, var. *sarawakensis*. This substance is dimorphic and melts at 189°, but when crystallised from acetone, melts at 192–194°. It has the formula $C_{23}H_{22}O_7$, and is isomeric with tephrosin and toxicarol. It is phenolic and is toxic, but as it is present in very small quantity its presence has little effect on the toxicity. Cahn and Boam consider that the state of knowledge of the constituents of derris resin may be summarised as follows. Rotenone and the new body melting at 189° occur free in the resin ; *dl*-toxicarol and at any rate part of the *dl*-deguelin do not occur as such. Not more than a small amount of the tephrosin occurs as such. Deguelin occurs, at least partly, either as the *l*-form or as its simple precursor. The remainder of the deguelin and tephrosin occur in some sort of combination or as simply related precursors. Nothing is known as to the mode of combination of the toxicarol. Cahn and Boam (J.S.C.I. 1935, **54**, 37T) consider that the determination of rotenone in derris roots is best effected in the following manner, but if the rotenone content of the resin is below 17% the results are too low.

The root should be powdered to pass a 50-mesh sieve and dried *in vacuo* before extraction. The root is extracted in a Soxhlet tube for 8 hours with trichlorethylene. The solvent is changed and a second extraction for 4 hours is made. If this extraction shows more than a faint yellow colour, a third extraction is made. The solvent is removed and the resin is dissolved in two parts of warm carbon tetrachloride saturated with rotenone. It is cooled, seeded if necessary, and allowed to stand overnight. The separated crystals are collected in a Gooch crucible, washed with CCl_4 saturated with rotenone, and dried below 50° in a current of air. The weight of the crystals×0·72 gives the weight of the rotenone. For fuller details the two papers by Cahn and Boam (*l.c.*) should be consulted.

Worsley (J.S.C.I. 1936, **55**, 349T) publishes a very lengthy series of analyses, and considers that the following points constitute improvements in the method of determining rotenone.

Ethyl acetate forms a very efficient solvent for the extraction of the rotenone. The higher the purity of the "rotenone complex" with carbon tetrachloride, the more accurate is the determination, and Worsley adds a given weight of pure rotenone to the extracted resins so as to bring their rotenone value to over 40%. The purity of the carbon tetrachloride complex prepared by Worsley's method is claimed to be, on the average, 94%, which is much higher than that prepared by Cahn and Boam. There are too many details in the methods for full reproduction here, so that the original papers must be consulted for these.

Tattersfield and Martin (J.S.C.I. 1937, **56**, 77T) have separated an optically active constituent of derris resin which they consider is an active precursor of toxicarol. It is uncertain whether the compound they obtained is in a high state of purity or not. The melting-point was 99° and the specific rotation in 4% benzene solution was −69°.

A useful account of the experimental work on the cultivation of *Derris elliptica*, *D. malaccensis*, and *D. thyrsiflora*, in Peradeniya, by Lester-James should be consulted (Bull. Imp. Inst. 1935, **2**, 199).

E. J. P.

DESALGIN. The proprietary name of a preparation containing 0·06% of chloroform in olive oil and peptone stated to have been employed as an analgesic in cases of gastric disorder (D. Ettinger, Pharm. Presse, 1929, **34**, 120).

DESCLOIZITE. A basic lead and zinc vanadate, $(Pb,Zn)_2(OH)VO_4$, crystallising in the orthorhombic system and isomorphous with olivenite (basic copper arsenate). A small amount of copper is usually present replacing zinc, and when this is present in larger amount the mineral grades into *cuprodescloizite*, which is identical with *mottramite* and *psittacinite* (F. A. Bannister, Min. Mag. 1933, **23**, 376). The crystals are deep reddish-brown to black in colour, and the streak is a paler yellowish-brown. It occurs in veins of lead ore in association with vanadinite, etc., and has been mined to a limited extent in New Mexico and Arizona, as a source of vanadium. It also occurs in considerable quantities in the Sierra de Cordoba in Argentina, and at Broken Hill in Northern Rhodesia. More recently it has been found in large amounts at several places in the Grootfontein district in South-West Africa.

L. J. S.

DESICHTOL. Trade name for ichthyol which, it is stated, has been deodorised without loss of therapeutic activity by treatment with steam (Pharm. Zentr. 1898, **39**, 90).

DESOXYCINCHONINE *v.* Cinchona Alkaloids (this vol., p. 158*c*).

DESOXYQUININE *v.* Cinchona Alkaloids (this vol., p. 177*d*).

DESPYRIN. Trade name for a preparation containing 14% of potassium bitartrate and 86% of acetylsalicylic acid (C. Mannich and G. Leemhuis, Apoth.-Ztg. 1913, **28**, 650).

DETERGENTS FROM PETROLEUM. The sulphonic acids produced in the refining of heavy fractions of petroleum have found considerable use as detergents. The sludges contain free acid, polymers, asphalts and a variety of sulphonates. On addition of water the free acid can be recovered and reconcentrated whilst the oily matter separates. From this the sulphonic acids can be recovered by extraction with a number of solvents. Other similar material can be obtained by the sulphonation of paraffin wax and its oxidation products.

Further halogenated sulphonic acids have been proposed. The sulphonic acids thus obtained are mixtures of some complexity. They each contain at least one sulphonic acid group, but the actual chemical structure of the hydrocarbon associated with it has not been determined. An average formula has been suggested of $C_{20}H_{27}SO_3H$. The sulphonic acid group is very firmly attached to the hydrocarbon nucleus. A large number of detergent substances are now available from this source, and in general it is the alkali metal salts that have been proposed for this purpose.

There is a considerable patent list concerned with petroleum detergents, and reference should be made to the very full article in Carleton Ellis's "Chemistry of Petroleum Derivatives." 1934.

A. E. D.

DETTOL. Halogen derivatives of xylenol dissolved in a saponified mixture of aromatic oils. It is a non-irritant and non-toxic germicide (*Reckitt & Sons, Hull*). B.P.C. 1934.

DEUTERIUM. **Introduction.**—Deuterium ^2H or D. A heavier isotope of hydrogen having an atomic weight 2·01363±0·00004 relative to helium 4·00216, and 2·01416 relative to oxygen 16 (Bainbridge, Physical Rev. 1933, **44**, 57; Wilson, Proc. Roy. Soc. 1936, A, **154**, 560). It is present in ordinary electrolytic hydrogen to the extent of 1 part in 30,000±20% (Bleakney, Physical Rev. 1932, **41**, 32; Bleakney and Gould, *ibid.* 1933, **44**, 265; *see also* Bradley and Urey, *ibid.* 1932, **40**, 889; Unsöld, Naturwiss. 1932, **20**, 936; Stern and Volmer, Ann. Physik, 1919, **59**, 225; Tate and Smith, Physical Rev. 1933, **43**, 672; Hardy, Barker, and Dennison, *ibid.* 1932, **42**, 279).

History.—The first indication of the existence of heavy hydrogen was given by atomic weight values. Aston, using the mass-spectrograph, obtained the value 1·00778±0·00015 for the mass of the hydrogen atom relative to $O=16{\cdot}000$. This is in agreement with the value $H=1{\cdot}00780$ obtained by chemical methods by Scott, Morley, Noyes, and Burt and Edgar.

After the discovery of the ^{18}O isotope and the abundance ratio $^{16}O:{}^{18}O$, Aston's value calculated to the chemical standard is $H=1{\cdot}00756$, so that the chemical value for ordinary hydrogen is higher by about 1 part in 5,000 than the true value for hydrogen consisting wholly of ^1H.

Birge and Menzel (Physical Rev. 1931, **37**, 1669) suggested that this discrepancy was due to the presence in ordinary hydrogen of a small amount of a heavier isotope ^2H; this fact has been established by subsequent workers. Urey, Brickwedde and Murphy (Physical Rev. 1932, **40,** 1) set out to concentrate the heavier isotope by evaporation of liquid hydrogen and obtained a residual liquid the Balmer spectrum of which showed clearly a line in the position for an atom of mass 2 and an atomic number 1. Washburn and Urey (Proc. Nat. Acad. Sci. 1932, **18,** 496), noted that there was a greater concentration of ^{2}H in the water from old electrolytic cells, and it is this discovery which has enabled the present extensive study of ^{2}H and its compounds to be made. Summaries of the earlier history of this matter are given in the following articles: Nature, 1933, **132,** 536; Rutherford, *ibid.* 1933, **132,** 955; 1934, **133,** 481.

Much discussion has taken place with regard to the names to be given to ^{1}H, ^{2}H, and possibly ^{3}H. The discoverers suggested protium, deuterium, and tritium respectively (Urey, Murphy and Brickwedde, J. Chem. Physics, 1933, **1,** 512), and these names are generally used. Rutherford, however, suggested diplogen for ^{2}H and diplon for the nucleus and the symbol D for the new isotope. Sidgwick supported this view (Proc. Roy. Soc. 1934, **144A,** 5). It is generally agreed that "hydrogen" should still be used for the mixture of all the isotopes and that the symbol for ^{2}H shall be D (*see* Urey, Brickwedde, and Murphy, Nature, 1934, **133,** 173).

Occurrence.—Every source of water so far examined shows the presence of heavy hydrogen, but it is difficult to secure an accurate measurement of the amount present. To reconcile the mass spectrograph atomic weight with the chemical value, hydrogen should contain about 1 part of ^{2}H in 4,500. Spectroscopic estimates are much lower, but were suspect owing to the marked tendency of H to be adsorbed in the discharge tube (Lewis and Spedding, Physical Rev. 1933, **43,** 964). Later estimates based on mass spectrographic measurements which are probably more reliable put the normal abundance ratio ^{1}H : ^{2}H at about 1 in 5,000 in rainwater (Bleakney, Gould, *ibid.* 1933, **44,** 265); for the method *see* Bleakney (*ibid.* 1932, **40,** 496; *also* Hardy, Barker and Dennison, *ibid.* 1932, **42,** 279; Tate and Smith, *ibid.* 1933, **43,** 672).

Perhaps the greatest obstacle to obtaining a true value of the abundance ratio is due to the large mass ratio (2 : 1) of the two hydrogen isotopes which, unlike other isotopes, gives rise to sufficient differences in physical and chemical properties as to facilitate partial separation during any process to which ordinary water may be subjected, *e.g.* distillation, electrolysis, etc. (*see* Washburn and Smith, J. Chem. Physics, 1933, **1,** 426; Edwards, Bell and Wolfenden, Nature, 1935, **135,** 793; Rakshit, J. Physical Chem. 1935, **39,** 303; Dole and Wiener, Science, 1935, **81,** 45; Christiansen, Crabtree and Laby, Nature, 1935, **135,** 870).

Hydrogen occurs for the most part in combination with oxygen as water, and precise determinations of the density of water from various sources have disclosed interesting variations. Water, prepared by the usual methods for conductivity experiments and in addition purified by established methods for density determinations, varied in density over a range of $5{\cdot}4\gamma d$ (one-millionth of the ordinary unit is called a gamma of density, $0{\cdot}000001d = 1\gamma d$), and so is unsuitable as a standard. London Thames water was found to be constant in density and this value agreed with that of surface waters from places so far apart as South Wales, Sumatra, and the U.S.A. Waters from the Dead Sea ($3{\cdot}0\gamma d$) and from a Tibetan lake at 13,500 ft. ($1{\cdot}5\gamma d$) are heavy, presumably owing to isotopic concentration by evaporation (Briscoe and others, J.C.S. 1934, 1207; 1937, 1492).

The concentration of heavy water in high altitude ice from Alpine glaciers frequently showed an increase, in some instances of as much as 50 to 100 (Baroni and Fink, Monatsh. 1935, **65,** 386; 1936, **67,** 193; 1937, **71,** 128; *see also* Eucken and Schäfer, Nachr. Ges. Wiss. Göttingen, Math. phys. Kl, III, 1935, **1,** 137; Riesenfeld and Chang, Ber. 1936, **69,** [B], 1305). Variations in the density of rain and snow water from various districts have been observed by Harada and Titani, Bull. Chem. Soc. Japan, 1935, **10,** 206, 263; Brodski, Skarre, Donzova and Slutzkaja, J. Physical Chem. Russ. 1937, **10,** 731. The water obtained by the combustion of cellulose and a number of other carbohydrates shows an enhanced concentration of deuterium (Harada and Titani, Bull. Chem. Soc. Japan, 1935, **10,** 205, 261, 465; Dole, J. Amer. Chem. Soc. 1936, **58,** 580).

The general conclusion from observations on the enrichment of deuterium oxide in waters obtained from natural sources is that such enrichment is comparatively small and is attributable to the operation of physical processes, *e.g.* preferential evaporation, freezing or diffusion.

Separation of the Isotopes.—(*a*) *Electrolytic Concentration of Deuterium Oxide.*—The production of large amounts of pure deuterium oxide is important from the research worker's point of view, and its possible technical applications have still to be explored. The most suitable process appears to be the electrolytic enrichment of ordinary water, and much work has been done in this direction in a relatively short time. Washburn and Urey (Proc. Nat. Acad. Sci. 1932, **18,** 496) showed that when dilute sulphuric acid is electrolysed using platinum electrodes a residual water having an increase in density of $164\gamma d$ was obtained after 98% of the water was decomposed. Further work was done by Lewis and MacDonald (J. Chem. Phys. 1933, **1,** 288, 341, 481); Washburn, Smith and Fransden (Bur. Stand. J. Res. 1933, **2,** 453; J. Chem. Phys. 1933, **1,** 288); Harkins and Doede (J. Amer. Chem. Soc. 1933, **55,** 4330); Harteck (Proc. Physical Soc. 1934, **46,** 277; Proc. Roy. Soc. 1934, **144A,** 1); Newell and Ficklen (J. Amer. Chem. Soc. 1933, **55,** 2167); Anderson, Holford and Bates (J. Chem. Phys. 1934, **2,** 342). Taylor, Eyring and Frost (*ibid.* 1933, **1,** 823), obtained 82 c.c. of 99% D_2O from 610 gallons of electrolytic liquor. This method with slight variations is the one generally employed in industry. $0{\cdot}5N$-sodium hydroxide is electrolysed between nickel or iron electrodes, the electrolyte being kept below 20°C. The process is carried out in about seven stages. In the first stage electrolysis proceeds until the volume is reduced to about 1/10, when the electrolyte has become concentrated in alkali and the process is stopped. About 9/10 of the electrolyte is treated with CO_2, distilled to dryness and the distillate added to the remaining 1/10 of the electrolyte, thus regaining approximately the original alkali concentration. This process of electrolysis and removal of alkali is repeated until the water has reached the desired degree of heaviness. Taylor, Eyring and Frost's results (*l.c.*) are given in the following table:

Water obtained from electrolysis No.	Density d_4^{20}	% Hydrogen which is heavy.
I	0·998	—
II	0·999	0·5
III	1·001	2·5
IV	1·007	8
V	1·031	30
VI	1·098	93
VII	1·104	99

A detailed account of a method using sulphuric acid and lead electrodes is described by Tronstad and Brun (Z. Elektrochem. 1934, **40**, 556). The efficiency of the concentration is remarkably insensitive to the conditions of electrolysis, and, although the separation factor has been the subject of extensive work, nothing sufficiently definite to have real significance has so far been forthcoming. Under apparently identical conditions different results have been obtained (*cf.* Tronstad and Brun, *l.c.*; *see also* Collie, Nature, 1934, **132**, 568 ; Bell and Wolfenden, *ibid.* 1934, **133**, 25 ; Proc. Roy. Soc. 1934, **144**A, 22 ; J.C.S. 1936, 286 ; Fowler, Proc. Roy. Soc. 1934, **143**A, 452 ; Erlenmeyer and Gärtner, Helv. Chim. Acta, 1934, **17**, 30, 1226 ; 1935, **18**, 419 ; Harteck, Proc. Roy. Soc. 1934, **144**A, 1 ; Oliphant, Nature, 1933, **132**, 675 ; Butler, Z. Elektrochem. 1938, **44**, 55 ; Eucken and Bratzler, Z. Physikal. Chem. 1935A, **174**, 273 ; Appleby and Ogden, J.C.S. 1936, 163 ; Brown and Daggett, J. Chem. Physics, 1935, **3**, 216 ; A. and L. Farkas, *ibid.* 1934, **2**, 468 ; Urey, Science, 1933, **78**, 566 ; Eyring, Proc. Nat. Acad. Sci. 1933, **19**, 78 ; Eyring and others, J. Chem. Physics, 1933, **1**, 345 ; J. Amer. Chem. Soc. 1933, **55**, 5058 ; J. Chem. Physics, 1934, **2**, 217 ; Nature, 1934, **133**, 291 ; Wolfenden and others, J.C.S. 1936, 286 ; 1937, 1677 ; Trans. Faraday Soc. 1938, **34**, 436).

(*b*) *Other Methods of Separation of Deuterium.*—Deuterium in ordinary hydrogen was first concentrated by utilising the difference in vapour pressure of the liquids. Brickwedde and Murphy (Physical Rev. 1932, **39**, 164, 864 ; **40**, 464) used this method and found that the relative abundance of deuterium in the last fraction was increased five or six times compared with the original gas. Keesom, van Dijk and Haantjes (J. Proc. Acad. Sci. Amsterdam, 1933, **36**, 248) used a specially designed rectifying column and obtained a sample containing 1·5% D_2. Taylor, Gould and Bleakney (Physical Rev. 1933, **43**, 496) record a small separation of isotopes by fractional desorption from charcoal. *See also* Washburn and Smith (J. Chem. Physics, 1933, **1**, 426), Lawson (Trans. Faraday Soc. 1936, **32**, 473); King and Lawson (*ibid.* 1936, **32**, 1). Hertz using his historic apparatus devised for the separation of neon isotopes, prepared pure deuterium by a fractional diffusion method, (Naturwiss. 1933, **21**, 884 ; *see also* MacGillavry, Rec. trav. chim. 1937, **56**, 330). *See* DIFFUSION, this vol., p. 605).

The diffusion of deuterium through palladium was investigated by A. and L. Farkas (Proc. Roy. Soc. 1934, **144**A, 467 ; Nature, 1933, **132**, 894) ; *cf.* Harris, Jost and Pearse (Proc. Nat. Acad. Sci. 1933, **19**, 991). Fractionation by diffusion through other metals was examined by Fink, Urey and Lake (J. Chem. Physics, 1934, **2**, 105) ; Jost and Widmann (Z. physikal. Chem. 1935, [B], **29**, 247) ; Luhr and Harris (Physical Rev. 1934, [ii], **45**, 843); Sieverts and Zapf (Z. physikal. Chem. 1935, **174**, 559).

The fractional distillation of water has been attempted by Washburn and Smith (J. Chem. Physics, 1933, **1**, 426) ; Lewis and Cornish (J. Amer. Chem. Soc. 1933, **55**, 2616) ; Hall and Jones (*ibid.* 1934, **56**, 749) ; Erlenmeyer and Gärtner (Helv. Chim. Acta, 1934, **17**, 970, 1008); Jaulmes (Chim. Ind. 1935, **33**, 1045); Stedman (Canad. J. Res. 1935, **13**B, 114) ; Hall and Jones (J. Amer. Chem. Soc. 1934, **56**, 749). Chemical methods were tried by Davis and Johnston (J. Amer. Chem. Soc. 1934, **56**, 492) ; Highes, Ingold and Wilson (J.C.S. 1934, 493).

The rapid conversion of deuterium oxide into deuterium by passing D_2O vapour over magnesium at 480°, giving a 95% yield, is described by Knowlton and Rossini (J. Res. Nat. Bur. Stand. 1937, **19**, 605).

Physical Properties of Deuterium.—Deuterium and its compounds differ in their physical and chemical properties from hydrogen and although, for the most part, these differences are small they are very definite.

The table at the head of the next page has been taken from the Z. Elektrochem. 1938, **44**, 22.

For other thermal properties, *see* Clusius and others (Nachr. Ges. Wiss. Göttingen. Math-phys. Kl., 1934, [ii], 1 ; Z. physikal. Chem. 1935, [B], **30**, 258 ; Physikal. Z. 1934, **35**, 969 ; Naturwiss. 1934, **22**, 526 ; Z. Elektrochem. 1935, **41**, 487 ; 1938, **44**, 21) ; Beutler (Z. Physikal. Chem. 1934, [B], **27**, 287) ; Scott, Brickwedde, Urey and Wahl (J. Chem. Physics, 1934, **2**, 454) ; Cleave and Maass (Canadian J. Res. 1935, **12**, 57, 372) ; Bijl (Nature, 1936, **138**, 723) ; Nothdurft (Ann. Physik. 1937, (v), **28**, 157) ; Megaw and Simon (Nature, 1936, **138**, 244) ; Archer (*ibid.* **138**, 286) ; Grew and Atkins (Proc. Phys. Soc. 1926, **48**, 415) ; Coppock (Trans. Faraday Soc. 1935, **31**, 913).

The normal potential of deuterium is given as 44 mv. by Abel and Redlich (Z. Elektrochem. 1938, **44**, 204). The overpotential at a mercury electrode in ordinary and heavy water has been investigated by Heyrovsky (Chem. Listy, 1937, **31**, 440) ; *see also* Bowden and Kenyon (Nature, 1935, **135**, 105).

The refractive index, n, for D_2 at λ 5462 is 1·0001378 assuming n for H_2 to be 1·00013966 (Orr, Trans. Faraday Soc. 1936, **32**, 1556) ; *see also* Larsén (Z. Physik. 1936, **100**, 543). Amdur (J. Amer. Chem. Soc. 1935, **57**, 588) found the viscosity of deuterium to be 1·414

	D_2	HD	H_2
Heat of vaporisation at 194·5 mm. Hg	302·3 cal.	263 cal.	219·7 cal.
Heat of sublimation at 0°Abs.	274·0 cal.	~228 cal.	183·4 cal.
Heat of fusion	47·0 cal.	37 cal.	28·0 cal.
θ-value for C_p (Debye)	89°	—	91°
θ-value for C_v (Debye)	97°	—	105°
M.p. Abs.	18·65°	16·60°	13·95°
B.p. Abs.	23·6°	—	20·38°
Triple point pressure mm. Hg	128·5	95	53·8
Depression of m.p. curve at triple point	40·5 kg./cm.^{2}	—	30·3 kg./cm.^{2}
Molecular vol. at triple point—liquid	23·14 cm.^{3}	—	26·15 cm.^{3}
Molecular vol. at triple point—solid	20·48 cm.^{3}	—	23·31 cm.^{3}
Zero point energy of the crystal	~215 cal.	~260 cal.	~305 cal.
Compressibility at 4·2°Abs.	$(3{\cdot}3\pm0{\cdot}7)10^{-4}$	—	$(5{\cdot}0\pm)10^{-4}$
Coefficient of expansion at triple point	0·08	—	0·12

times that of hydrogen. Keyes has calculated η for hydrogen by the method of least squares and finds $\eta=91{\cdot}6$ c.g.s. units at 30°, therefore for D_2 $\eta=\sqrt{2}\times 91{\cdot}6=129{\cdot}5$ c.g.s. units.

Torrey (Physical Rev. 1935, [ii], **47**, 644), using Rankine's method, gets $\eta_D:\eta_H=1{\cdot}410\pm0{\cdot}03$. *See also* van Cleave and Maass (Canadian J. Res. 1935, **13**, B, 384).

Vapour pressure of HD and D_2 was measured by Brickwedde and others (Physical Rev. 1934, [ii], **45**, 565 ; 1935, [ii], **48**, 483) ; Steiner (Z. Physik, 1932, **79**, 601) ; A. and L. Farkas and Harteck (Physikal. Z. 1936, **37**, 447); Bartholomé and Eucken (Z. Elektrochem, 1936, **42**, 547) ; the following table is taken from Z. Elektrochem. 1938, **44**, 23.

T° Abs.	V.P. in mm. Hg.	
	H_2	D_2
15	96·6	12·6
16	155·4	25·9
17	237·7	49·4
18	348·7	88·2
19	493·7	146·3
20	678·3	221·0

For the adsorption of hydrogen isotopes on carbon, copper, lead, nickel and other surfaces, *see* Barrer (Trans. Faraday Soc. 1936, **32**, 481) ; Beebe and others (J. Amer. Chem. Soc. 1935, **57**, 2527) ; Maxted and Moon (J.C.S. 1936, 1542) ; Magnus and Sartori (Z. physikal. Chem. 1936, A, **175**, 329) ; Lennard-Jones and others (Proc. Roy. Soc. 1935, A, **150**, 442 ; 1936, A, **156**, 16) ; Pace and Taylor (J. Chem. Physics, 1934, **2**, 578) ; Klar (Naturwiss. 1934, **22**, 822; Z. physikal. Chem. 1935, **174**, 1) ; Kohlschütter (*ibid.* 1934, **170**, 300) ; Melville and Rideal (Proc. Roy. Soc. 1935, A, **153**, 77, 89) ; Hudson and Ogden (Nature, 1938, **142**, 476).

General Reactivity of Deuterium.—Deuterium differs from hydrogen in its chemical reactivity. These differences are sometimes considerable, as is shown by the velocity constant data given in Table A on p. 564. See Geib, Z. Electrochem. 1938, **44**, 86, for bibliography and fuller details.

Compounds of Deuterium.—The most completely studied compound of deuterium is the oxide, D_2O. Its more important physical constants are given in Table B on p. 564.

For the diamagnetism of D_2O, *see* Gray and Cruickshank (Nature, 1935, **135**, 268) ; Specchia and Dascola (Nuova Cim. 1935, **12**, 606).

For dissociation constants of deuterium oxide and of electrolytes dissolved in it, *see* Schwarzenbach (Z. Elektrochem. 1938, **44**, 46) ; reaction velocity, Reitz (*ibid.* 1938, **44**, 72) ; thermal properties and dissolving power, Lange (*ibid.* 1938, **44**, 31).

Reactions in Deuterium Oxide—The substitution of deuterium oxide for water affects the reaction velocity in three principal ways:

1. In the majority of instances so far investigated the effect of heavy water has been to reduce the rate of reaction in solution by as much as 20%. The velocity of a reaction depends to a far-reaching extent on the solvent used, even when this takes no active part in the reaction. That there is connection between such physical properties as viscosity, dielectric constant, etc., of the solvent and its influence on the course of a reaction is evident although it has not been possible, so far, to decide as to the quantitative effect of any particular factor.

2. The interchange between hydrogen atoms of the reactant and deuterium atoms in the water is a further cause of change in reaction velocity. In aqueous solution this interchange is in many instances instantaneous and complete (*e.g.* $NH_3+D_2O\rightleftharpoons ND_3+H_2O$), with the result that there is a change in the nature of the reacting substances. In other cases interchange takes place in varying extents and rates depending on the experimental conditions, as is notably the case with hydrogen linked to carbon. In general the ultimate effect is a slowing down of the reaction velocity.

3. The third effect is produced when deuterium oxide itself takes part in the reaction either as D_2O molecules or in the form of D or OD ions. In this instance the reaction is by no means always retarded ; for the most part an acceleration is observed. This is notably the case in acid catalysis and frequently with bases. For a detailed account of reaction velocities in deuterium oxide and bibliography, *see* Reitz, (Z. Elektrochem. 1938, **44**, 72).

Electrolytic dissociation is in general less in D_2O than in H_2O. Typical values are given in Table B, p. 564, but for theoretical treatment of the results obtained together with references

TABLE A.

Reactions compared.	Temp. °C.	Vel. const., k_1/k_2.	Difference in kg.-cal. Active energy, Q_1-Q_2.	Difference in kg.-cal. Zero point energy, $E_1^0-E_2^0$.
$\frac{\mathrm{H+H+(M)}^*}{\mathrm{D+D+(M)}}$	20	1·4	0	0
$\frac{\mathrm{H+H_2}}{\mathrm{D+D_2}}$	630–710	1·85 (mean)	0·52	1·8
$\frac{\mathrm{D+H_2O}}{\mathrm{H+D_2O}}$	183 (wall reaction) ?	~1·7	~0·75	3·6
$\frac{\mathrm{D+NH_3}}{\mathrm{H+ND_3}}$	260–400	3·2–2	1·5	5·6
$\frac{\mathrm{D+PH_3}}{\mathrm{H+PD_3}}$	420–620	1·04	0·6	4·3
$\frac{\mathrm{H+HCl}}{\mathrm{D+DCl}}$	—	—	0·6	1·2
$\frac{\mathrm{Na+ClH}}{\mathrm{Na+ClD}}$	238	1·33	0·35	1·2
$\frac{\mathrm{Cl+H_2}}{\mathrm{Cl+HD}}$	30	3·3	0·6	0·8
$\frac{\mathrm{Cl+HH}}{\mathrm{Cl+DD}}$	0 and 30	13·4 and 9·75	1·2	1·8
$\frac{\mathrm{Br+HH}}{\mathrm{Br+DD}}$	275–380	5·5–4·4	1·5	1·8
$\frac{\mathrm{I_2+H_2}}{\mathrm{I_2+D_2}}$	425–500	2·45–2·1	0·75	1·8
$\frac{\mathrm{2HI}}{\mathrm{2DI}}$	430	1·53	0·6	2·093
$\frac{\mathrm{C_2H_4+H_2}}{\mathrm{C_2H_4+D_2}}$	530–570	2·5	0·95	1·8

* M is the third body necessary for the occurrence of such a reaction in the gas phase.

TABLE B.

	H_2O	D_2O
Crystalline structure	a=4·525 A c=7·39	a=4·505 A c=7·36
Density, d_4^{25}	0·99705	1·1048
Relative molecular vols. at 20°	1·0037	1
M.p.	0°C.	3·8°C.
B.p.	100°C.	101·42°C.
Temperature of max. density	4°C.	11·6°C.
Heat of sublimation (triple point)	12170 cal./mol.	12631 cal./mol.
Heat of fusion	1435 cal./mol.	1523 cal./mol.
Dielectric const. 0°C.	81·5	80·7
Mol. magnetic susceptibility 20°	$12·96\times10^6$	$12·97\times10^6$
Surface tension 12°C.	73·7 dynes/cm.	73·8 dynes/cm.
Viscosity 25°C.	0·891 centipoises	1·0992 centipoises
Refractive index, n_D^{20}	1·33300	1·32844

Ionic mobilities, T=18°C.			
Solvent 97% D_2O	D^+ 213·7	K^+ 54·5	Cl^- 55·3
Solvent H_2O	H^+ 315·2	K^+ 64·2	Cl^- 65·2
Solubility 25°C. g./100 g. solvent			
Solvent D_2O	NaCl 305	$BaCl_2$ 289	(20°C.)
Solvent H_2O	NaCl 359	$BaCl_2$ 357	(20°C.)
Electrolytic dissociation			
D_2O $K_{D_2O}=0·16\times10^{-15}$	$K_{H_2O}=1·6\times10^{-15}$		
HDO $[D^+]=0·111\times10^{-7}$	$[H^+]=0·564\times10^{-7}$		

to the literature, *see* Schwarzenbach (Z. Elektrochem. 1938, **44**, 46).

Substance.	Dissocn. Const. in H_2O / Dissocn. Const. in D_2O at 20° C.
HSO_4^-	2
$H{\cdot}COOH$	2·50
$CH_3{\cdot}COOH$	2·87
Hydroquinone	3·36

Salts having water of crystallisation can have one or more of the molecules of water replaced by a corresponding number of molecules of D_2O. Research on the deuterates of $CuSO_4$ has been carried out by Partington and Stratton (Nature, 1936, **137**, 1075) ; Mules and Menzies (J. Amer. Chem. Soc. 1938, **60**, 87), and by Perpérot and Schacherl (J. Phys. Radium, 1935, **6**, 439). Taylor (J. Amer. Chem. Soc. 1934, **46**, 2634) found the transition temperature of $Na_2SO_4{,}10D_2O$ to be 34·48°±0·02° as against 32·38°±0·001° for the corresponding hydrate. Bell (J.C.S. 1937, 459) measured the dissociation pressure of a number of deuterates, *e.g.* $CuSO_4{,}5D_2O$; $SrCl_2{,}6D_2O$, *etc.* Godchot, Cauquil and Calas (Compt. rend. 1936, **202**, 759) obtained the deuterates of krypton and xenon with $6D_2O$.

Other Inorganic Compounds of Deuterium.—These can for the most part be prepared by several general methods slightly modified to suit individual cases.

1. *Acids*, by action of D_2O on the acid anhydride, *e.g.* D_2SO_4 (Ingold and others, J.C.S. 1936, 916).
2. *Non-Metallic Deuterides*, from the elements with or without a suitable catalyst, *e.g.* DBr or by the action of D_2O on a suitable salt, *e.g.* D_2S from $Al_2S_3+D_2O$; ND_3 from $Mg_3N_2+D_2O$.
3. Interchange reaction with or without a suitable catalyst (*v. infra*).
4. Action of D_2O on the metal yields deuteroxides in the case of some metals, *e.g.* NaOD.

For a detailed account of inorganic deuterium compounds and a bibliography, *see* Erlenmeyer (Z. Elektrochem. 1938, **44**, 8).

Some typical differences in the physical properties of corresponding deuterium and hydrogen compounds are shown in the following table :

Compound.	M.p. absolute	B.p. absolute	Latent heat of evapn. cal./mol.	Critical temp.
HCl	162·2	188·1	4081	51·0
DCl	158·2	191·6	4151	50·3
HBr	186·2	206·3	4257	89·9
DBr	185·7	206·3	4258	88·8
HI	222·3	237·5	4724 ?	150·7
DI	221·5	237·0	4713 ?	148·6
NH_3	195·3	239·8	5797	132·5
DH_3	199·6	242·1	5990	132·3
HCN	259	298·5	6600	—
DCN	261	299·1	6500	—

Organic Compounds of Deuterium.—The preparation of organic compounds of deuterium may be carried out by a large variety of preparative methods, many of which are exactly parallel to the general methods of preparation of the corresponding hydrogen derivatives.

Examples of these are :

1. Treatment of carbides with D_2O.
2. Catalytic deuterisation.
3. Grignard reactions.
4. Addition of D_2 under suitable conditions.
5. Exchange reactions.

The following are examples illustrative of some of these methods :

Tetradeuteromethane, CD_4, is prepared by the reaction of D_2O with aluminium carbide (Urey and Price, J. Chem. Physics, 1934, **2**, 300).

Mono deutero-tetramethylmethane,

$$(CH_3)_3C{\cdot}CH_2D,$$

was prepared from D_2O and the Grignard compound of 1-chlor-2:2-dimethylpropane, (Whitemore, Fleming, Rank, Bordner and Larsén, J. Amer. Chem. Soc. 1934, **56**, 749, 934). For a comprehensive bibliography up to January, 1938, *see* Erlenmeyer (Z. Elektrochem. 1938, **44**, 9).

Differences in melting-point and boiling-point of corresponding deutero- and hydrogen organic compounds are shown in the following table :

Substance.	M.p. °C.	B.p. °C.
C_6H_6	5·5	80·1
C_6D_6	6·8	79·4
$C_{10}H_8$	80·2	
$C_{10}D_8$	77·5	
$CH_3{\cdot}CHO$	−123·5	20·2 (760)
$CD_3{\cdot}CDO$	−121·7	20·5 (756)
$(CH_3{\cdot}CHO)_3$	10·5	124 (760)
$(CD_3{\cdot}CDO)_3$	13·7	124 (753)
$CH_3{\cdot}COOH$	16·6	
$CH_3{\cdot}COOD$	15·4	
$CD_3{\cdot}COOH$	17·2	
$CD_3{\cdot}COOD$	15·9	
CH_4	−90·6	
CD_4	−89·2	

Interchange Reactions.—These may be divided into two classes, homogeneous and heterogeneous.

Homogeneous Reactions.—A number of substances containing hydrogen exchange one or more of their hydrogen atoms for deuterium when dissolved in D_2O. Certain of these are obviously ionic reactions and, as such, occur very rapidly, *e.g.* on dissolving sodium hydroxide in deuterium oxide interchange occurs instantaneously according to the equation :

$$NaOH+D_2O \rightleftharpoons NaOD+HDO$$

This exchange can be followed quantitatively by recovering the diluted D_2O subsequently and determining its density. In a mixture of H_2O and D_2O the available deuterium distributes itself between solvent and solute in proportion to the molecular quantities of each present. For the most part the exchange reactions of deuterium occur very rapidly, in other cases the exchange takes place with measurable velocity, and an analysis of the kinetics of such reactions shows that the ionic reaction of hydrogen interchange itself must be preceded by some intermediate reaction the velocity of which determines the rate of the whole reaction. Amongst slow inorganic interchange reactions the exchange of hydrogen in complex salts should be noted. Hexamminecobaltic chloride, for instance, interchanges its hydrogen for deuterium and it has been found that the reaction velocity is inversely proportional to the hydrogen ion concentration. This discovery is of importance in studying the theory of complex salts (*see* Erlenmeyer and Gärtner, Helv. Chim. Acta, 1934, **17**, 1008 ; Bankowski, Monatsh. 1935, **65**, 266 ; James, Anderson and Briscoe, Nature, 1937, **139**, 109 ; Anderson, Spoor and Briscoe, *ibid.* 1937, **139**, 508 ; Garrick, *ibid.* 1937, **139**, 507).

Bonhoeffer and Brown (Z. physikal. Chem. 1933, B, **23**, 172) were the first to discover the interchange phenomenon. They found that NH_4Cl dissolved in D_2O exchanged all its hydrogen atoms, and this reaction has been utilised to obtain water free from deuterium. It has been found that hydrogen which is linked to oxygen, nitrogen, sulphur or halogen readily interchanges with deuterium. Since then it has been determined that many other substances, *e.g.* glycol, hydrogen peroxide, acetoacetic ester, phenols, etc., exchange one or more hydrogen atoms more or less readily according to the conditions of experiment. For bibliography, *see* Ingold and Wilson (Z. Elektrochem. 1938, **44**, 70).

A limited number of interchange reactions occur with deuterium atoms in the gaseous phase. The source of such atoms may be the electric discharge, photochemical excitation by means of mercury resonance radiation, or thermal dissociation of heavy water molecules with formation of atomic deuterium (Geib and Steacie, Z. physikal. Chem. 1935, B, **29**, 215 ; Steacie and Phillips, J. Chem. Physics, 1936, **4**, 461 ; Trenner, Taylor and others, *ibid.* 1937, B, **5**, 28, 203, 212 ; Farkas and others, Nature, 1933, **132**, 892 ; J.C.S. 1936, 26 ; Proc. Roy. Soc. 1936, **157**, A, 625).

Heterogeneous Interchange.—Interchange of hydrogen isotopes between simple molecules is catalysed by the common hydrogenation catalysts such as platinum, palladium, nickel, iron, etc. (Farkas, and Farkas and others, Trans. Faraday Soc. 1935, **31**, 821 ; 1936, **32**, 416, 922 ; J. Amer. Chem. Soc. 1938, **60**, 22 ; Taylor and others, *ibid.* 1935, **57**, 660, 1256 ; 1936, **58**, 1445 ; 1938, **60**, 362 ; Hirota and Horiuti, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **30**, 151 ; Horiuti and Polanyi, Trans. Faraday Soc. 1934, **30**, 1164 ; *see also* Ingold and Wilson, Z. Elektrochem. 1938, **44**, 62).

Biological Applications.—The use of deuterium as an indicator in the study of intermediary metabolism has produced much useful information. von Hevesy and Hofer (Nature, 1934, **134**, 879) used deuterium oxide to follow the elimination of water from the human body. Erlenmeyer and Gärtner (*ibid.* 1006) examined its distribution in rats. Breusch and Hofer (Berlin. klin. Woch. 1934, **13**, 1815) found that no fractionation of H_2O and D_2O in the organism could be detected in normal cases. Woglom and Weber (J. Amer. Chem. Soc. 1934, **104**, 1289) showed that D_2O has no effect on mouse sarcoma. Deuterium has been used as an indicator in fat and other metabolism (Cavanagh and Raper, Nature, 1936, **137**, 233 ; Rittenberg and others, J. Biol. Chem. 1936, **114**, 381 ; **115**, 635 ; 1937, **117**, 485).

The incorporation of deuterium in the living organism is the subject of a research by Bonhoeffer and others (Z. physikal. Chem. 1936, **175**, 459 ; **176**, 202 ; 1937, **180**, 185).

The effect of exchange of deuterium for hydrogen in experiments involving enzymes and moulds is to produce a greater or less reduction in activity. Pollen germinates more slowly in D_2O than in ordinary water (Plantefol and Champetier, Compt. rend. 1935, **200**, 423). Yeast is less active in presence of deuterium oxide (Taylor and Harvey, Proc. Soc. Exp. Biol. Med. 1934, **31**, 954 ; *cp.* Hughes, Yudkin, Kemp and Rideal, J.C.S. 1934, 1105 ; Steacie, Z. physikal. Chem. 1934, B, **27**, 6 ; Bonhoeffer and Salzer, Naturwiss. 1935, **23**, 867 ; Shoup and Meyer, J. Tennessee Acad. Sci. 1935, **10**, 127 ; Salzer and Bonhoeffer, Z. physikal. Chem. 1936. **175**, 304 ; von Dungern, Z. Biol. 1936, **97**, 187).

A summary of researches in physiological chemistry using deuterium compounds is given by Bonhoeffer (Z. Elektrochem. 1938, **44**, 87) and Theis (Woch. Brau. 1938, **55**, 36).

Spectroscopic Data.—The wave-lengths of chief lines in the Balmer series of deuterium are given below, the bracketed data being values for the corresponding $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$ lines. $D\alpha$ 6561·00 (6562·793) ; $D\beta$, 4860·00 (4861·326) ; $D\gamma$, 4339·282 (4340·467), and $D\delta$ 4100·619 (4101·738). The differences between deuterium and hydrogen in the Balmer series are in agreement with the calculations of the isotope effect based on the Rydberg formula.

The molecular spectra of HD and D_2 have been studied and the differences between these molecules and hydrogen accord with calculations based on the theory of the isotope effect. The spectra of the numerous other diatomic molecules have also been examined (*e.g.* LiD, NaD, AgD, CaD, AlD, etc.). For data, *see* "Tables Annuelles de Constantes et Données Numériques. I Deuterium et Composés de Deuterium," by G. Champetier (Hermann & Cie, Paris), 1937.

The general effect of substitution of deuterium for hydrogen is to change the features of the spectrum dependent on the moment of inertia of the molecule. The interatomic distance is not altered by substitution of D for H. The change in the moment of inertia may have profound effect on the general appearance of the spectrum. Thus the ultra-violet absorption spectra of the molecules ND_3 and NH_3 or of $CH_3{\cdot}ND_2$ and $CH_3{\cdot}NH_2$ are quite distinct, as are the infra-red spectra of molecules such as DCl and HCl or D_2O and H_2O. These distinctions have also been observed in the Raman spectra of a large number of substances, C_6H_5D and C_6H_6 or $CH_3{\cdot}COOD$, $CH_3{\cdot}CO_2H$ and $CD_3{\cdot}CO_2D$. For comprehensive data, *see* Champetier, *op cit.*). The table below illustrates typical changes in the fundamental frequencies of molecules brought about by substitution of **D** for **H**.

Molecule.	Fundamental frequencies, cm.$^{-1}$
H_2S	2578
D_2S	1875
H_3As	2094
	990
	910
D_3As	1508
	730
	630

In the case of more complex molecules (*e.g.* with C_6H_6 or $CH_3{\cdot}COOH$) partial substitution of hydrogen by deuterium has been used as a means of assigning observed vibrational frequencies to the appropriate molecular vibration.

Estimation of Deuterium.—A number of methods are in use for the estimation of D, some of which can be applied only to water and others only to gaseous hydrogen.

Spectroscopic and Mass Spectrographic Methods.—These methods are qualitative as well as quantitative. The first quantitative estimation of deuterium was carried out spectroscopically by Urey, Brickwedde and Murphy (Physical Rev. 1932, **39**, 164, 864). The method was based on the different wave-lengths of the corresponding lines in the atomic spectra of the hydrogen isotopes and was carried out by comparison of the intensities of the β and γ lines of the Balmer spectrum. Bleakney (*ibid.* 1932, **40**, 496 ; **41**, 32 ; 1933, **44**, 265 ; 1934, **45**, 281, 655) devised a very accurate method using the mass spectrograph and which required only small quantities of gas.

A thermo-conductivity-micro method was employed by Farkas for which 2–3 cu. mm. of gas were required. The D content, however, must not be less than 1%. It has an accuracy of ±0·1% (*see* Farkas, Proc. Roy. Soc. 1934, **144**, A, 467; Trans. Faraday Soc. 1936, **32**, 413; Farkas, Farkas and Rideal, Nature, 1936, **137**, 315 ; *see also* Harteck, Z. Elektrochem. 1938, **44**, 3).

The most widely used method of estimating deuterium is that depending on the direct determination of the density of water containing deuterium either by the pyknometer or by means of the float, each of which is capable of an accuracy of 1 in 10^{-6}. This method is applicable to the determination of D_2 in all compounds which can be oxidised to give water. For details of the pyknometric method, *see* Washburn and others (J. Res. Bur. Stand. 1933, **11**, 453 ; 1934, **12**, 305). For the float method, *see* Lewis and MacDonald (J. Chem. Phys. 1933, **1**, 341); Emeléus, James, King, Pearson, Purcell and Briscoe (J.C.S. 1934, 1207 ; 1935, 1545).

Bibliography.—A. Farkas, " Orthohydrogen, Parahydrogen, and Heavy Hydrogen," University Press, Cambridge, 1935 ; G. Champetier, " Tables Annuelles de Constantes et Données Numériques. I. Deuterium et Composés de Deuterium," Paris, 1937.

M. C.

DEVARDA'S ALLOY. A brittle alloy containing 45% of aluminium, 50% of copper, and 5% of zinc. Devarda's alloy reduces nitrates to ammonia quantitatively in alkaline solution, the ammonia being then distilled into standard acid solution (Devarda, Chem.-Ztg. 1892, **16**, 1952 ; Z. anal. Chem. 1894, **33**, 113 ; Busvold, Chem.-Ztg. 1914, **38**, 799) (*v.* CHEMICAL ANALYSIS, Vol. II, pp. 598, 664).

DEXTRAN, $C_6H_{10}O_5$, or *viscose*, is a gum which occurs in the unripe sugar beet (Scheibler, Wag. J. 1875, 790). It is formed in the lactic fermentation of cane sugar by the action of *Streptococcus* (*Leuconostoc*) *mesenteroïdes*, (van Tieghem, Jahresber. Agric. Chem. 1879, 544 ; Béchamp, Compt. rend. 1881, **93**, 78; Brüning, Annalen, 1857, **104**, 197). *S. hornensis* isolated from curdled milk, some water samples and flowers also converts media containing up to 20% sucrose into dextran (Boekhout, Centr. Bakt. 1900, [ii], **6**, 161).

An animal dextran, $C_6H_{10}O_5$, is found in the galls produced on elms by the louse (*Schizoneura lanuginosa*) (Liebermann, Pflüger's Archiv. **40**, 454).

DEXTRINS, $n(C_6H_{10}O_5)$. When diastase acts on starch paste, maltose is the principal product, but various dextrins are also formed, their nature depending on the nature of the enzyme and the conditions of action. The precise nature of these products of the degradation of starch still remains obscure and it is not easy to make a satisfactory review of the subject at the present time. Recent work, however, points strongly in the direction of the dextrins being *side products* or *by-products* of the action of enzymes on starch rather than, as previously believed, intermediate products formed on the way to maltose. The dextrins differ according to the conditions (p_H, temperature, concentration) and the nature of the enzyme used. Some (like α-amylodextrin) appear to be fragments of the original starch molecule left unattacked by the enzyme preparation. Others appear to be formed owing to reversion or retrogradation occurring (stable dextrins).

According to their behaviour towards iodine they have been classed into :[1]

Amylodextrins, giving a blue colour and soluble in 25% alcohol.

Erythrodextrins, giving a reddish-brown colour and soluble in 55% alcohol.

Achroodextrins, showing no colour and soluble in 70% alcohol.

In the following a summary is given of the more definite dextrins which have significance in regard to the structure of starch and the mode of action of the two amylases (the α- and β-amylases of recent workers).

Unfortunately Syniewski, whose work perhaps forms one of the best contributions to the subject, has used a different and special nomenclature. Especially interesting in Syniewski's work is the proof that ungerminated barley is actually richer in diastase (his α-diastase) than the malt made from it. This diastase, however, is present in a form which is insoluble in water and is only brought out by digestion with a protease—*papayotin* ; during germination the barley amylase is apparently released and partly converted into the second amylase (his β-diastase). He shows how the two diastases augment each others' activity, and works out a quantitative method for measuring this effect.

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[1] An account of starch-iodine coloration as an index of differential degradation by the amylases has been given by C. S. Hanes and M. Cattle. Proc. Roy. Soc. 1938, B, **125**, 387–414.

The dextrins are characterised physically by their optical rotation and cupric reducing power.

The early work of Brown, O'Sullivan, etc., gave the reducing values (K) in terms of glucose taken as 100. Later values were expressed in terms of maltose as 100 by the symbol R, or preferably R_M.

In Germany and the U.S.A., the Wein method and tables (" Tabellen zur quantitativen Bestimmung der Zuckerarten," 1888) are still used in estimating maltose in spite of the fact that British workers since 1897 have shown them to be incorrect to the extent of being 5% low for anhydrous maltose (Brown *et al.*, J.C.S. 1897, **71**, 103–106 ; Ling and Baker, *ibid.* 509).

Syniewski since 1925 has used corrected Wein values.

I. THE SO-CALLED AMYLODEXTRINS (PRODUCING A PURE BLUE COLOUR WITH IODINE) (NON-REDUCING).

A.—The so-called "**amylodextrin**" or **solubilised starch** (Syniewski, Annalen, 1902, **324**, 212 ; 1925, **441**, 277), is made from potato starch by heating with water in an autoclave (12 hours at 140°C.) until it is completely soluble.

It has the composition $C_{216}H_{372}O_{186}$, and was regarded by Syniewski as 12 maltose radicals combined with a dextrin-ring complex.

B.—α-**Amylodextrin**, $[\alpha]_D$ 190–195°, R_M= 0·56–2 (J. L. Baker, J.C.S. 1902, **81**, 1177), is prepared by the action of precipitated diastase from barley extract (*i.e.* the α-amylase of Syniewski, Biochem. Z. 1925, **158**, 87) on Lintner's soluble starch, or on starch paste, preferably at 50° C. (The action on starch paste is slower than that on soluble starch.) It is sparingly soluble in cold water, readily in hot water. Solutions give a pure blue colour with iodine. It is converted by precipitated *malt* diastase after 18 hours' action into maltose, achroodextrin, and a considerable amount of glucose.

C. **Non-reducing Limit-dextrin I (Grenz-dextrin I)**, $[\alpha]_D^{20}+194\cdot92°$, R =0·97 (Syniewski, Annalen, 1925, **441**, 285; he was unaware of J. L. Baker's work). Prepared by the action of barley extract (*i.e.* the α-amylase of Syniewski, Biochem. Z. 1925, **158**, 87) on his amylodextrin solutions (5·7%) at ordinary temperature in 75 minutes ; action then became very slow.

The slight reducing power is regarded as due to decomposition of the dextrin by hot Fehling's solution.

It gives a pure blue colour with iodine solution. Analysis indicated :

$$C_{72}H_{126}O_{63} \text{ or } (C_6H_{10}O_5)_{12},3H_2O.$$

It polymerises in cold aqueous solution to $3(C_{72}H_{126}O_{63})$, and the molecular weight by the F.P. method gives 6,002 (Theory 5,997). It is converted by malt extract previously heated at 76°C. into 67·3% maltose and the reducing Limit-dextrin I ($[\alpha]_D$=180°).

The α-amylodextrin of Baker or non-reducing Limit-dextrin I of Syniewski would be the α-starch of Van Klinkenberg (Erg. Enzymforsch. 1934, **3**, 71) left unattacked by his β-diastase.

The above substances must be distinguished from Nägeli's amylodextrin (1874), which is obtained by the *very prolonged* action of acids on potato starch at the ordinary temperature. This, according to Brown and Morris (J.C.S. 1889, **55**, 449) is easily soluble in hot water, dissolves in cold water to form a 1·75% solution, and produces an *intense-red* coloration with iodine. It had $[\alpha]_{j\,3\cdot86}=206\cdot3°$, $K_{3\cdot86}=9\cdot07$, and was *completely converted* into maltose by malt extract in 20 minutes, at temperatures up to 60°C. This dextrin was a strongly reducing substance.

Lintner and Düll's "*amylodextrin*" (Ber. 1893, **26**, 2533) or "amorphous soluble starch" had $[\alpha]_D=196°$ and was non-reducing and apparently the same as Baker's and Syniewski's material.

II. REDUCING DEXTRINS—" LIMIT-DEXTRINS " (GRENZ-DEXTRIN).

D.—**Limit-dextrin I**, $[\alpha]_D^{20}+179\cdot6°$, $R_M=17\cdot65$ (Wein) [1] and 16·2° (Wein) (Syniewski, Annalen, 1899, **309**, 282; 1902, **324**, 212), is prepared by the action of fresh malt extract on starch paste at ordinary temperatures, and also on solutions of amylodextrins.

Analysis indicates :

$$C_{72}H_{124}O_{62}=12(C_6H_{10}O_5),2H_2O.$$

Mol. wt. found=1,897 (F.P.). (Theory=1,980.)

When treated with malt extract for a very long period (three weeks in 5% solution) it gave "*iso*maltose," which was extremely hygroscopic, $[\alpha]_D^{20}=+141\cdot4°$, $R_M=84\cdot5$ (Wein), osazone, m.p. 152·5°.

Syniewski terms this *iso*maltose " dextrinose."

E.—**Limit-dextrin II**, $[\alpha]_D+179\cdot6°$, $R_M=30\cdot0$ (Wein) (Syniewski, Annalen, 1902, **324**, 212), is made by the action of malt extract previously heated for 15 minutes at 76–77°C. (this would be by the action of the β-diastase of Syniewski, the α-diastase of others) on solubilised starch, until the iodine colour just disappears. Analysis indicated :

$$C_{36}H_{62}O_{31}=6(C_6H_{10}O_5),H_2O$$

Mol. wt. found=1,039. (Theory=990.)

It dissolves fairly readily in hot 80% alcohol, sparingly in 90% alcohol, and is converted slowly by unheated fresh malt extract (45°C., 48 hours) though nearly quantitatively to maltose (99·0% Wein=104% corrected).

This is *identical* with the following dextrins of other workers :

E_1.—**Maltodextrin**, $[\alpha]_{j\,3\cdot86}=193\cdot1°$, $K_{3\cdot86}=21\cdot1$ (Brown and Morris, J.C.S. 1885, **47**, 527), made by the action of freshly prepared diastase from green malt on starch paste at 60–65°C. (This would be the action of the β-diastase of Syniewski, the action being carried to $[\alpha]_{j\ 3\cdot86}=198°$.)

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[1] In his early papers, Syniewski used the Wein method for determining maltose, which gives results about 5% low. The values given marked (Wein) are his values. In later papers he made correction for the Wein error.

Brown and Millar (*ibid.* 1899, **75**, 286) give the equivalent $[\alpha]_D=180°$, $R_M=34\cdot5$.

It was regarded as $C_{12}H_{22}O_{11}<(C_{12}H_{20}O_{10})_2$ and was said to be completely convertible by fresh diastase into maltose.

E_2.—**Maltodextrin-α**, $[\alpha]_D$ 180°, $R_M=32\cdot8$ (Ling and Baker, *ibid.* 1897, **71**, 508), was made by the action of precipitated malt diastase on starch paste at 70°C., and had the formula $C_{36}H_{62}O_{31}$, mol. wt. found 990.

It is sparingly soluble in 80% alcohol, and is said to be incompletely converted to maltose by precipitated malt diastase. (After 48 hours at room temperature the conversion had $[\alpha]_{D\ 3\cdot93}=141\cdot3°$, $R_{3\cdot93}=90\cdot8$.)

E_3.—**Achroodextrin II**, $[\alpha]_D$ 183°, $R_M=26\cdot5$–$26\cdot8$ (Lintner and Düll, Z. ges. Brauw. 1894, **17**, 339), was separated from starch conversions. They regard Brown and Morris's maltodextrin as a mixture of achroodextrin II and "*iso*maltose."

III. Simpler Dextrins.

F.—**γ-Maltodextrin**, $[\alpha]_D$ 172·28° (8·5% solution), $R_M=42\cdot7$ (Wein) (Syniewski, Annalen, 1902, **324**, 212), made by fresh malt extract acting on Limit-dextrin II for one hour until the product shows 60% apparent maltose and then fractionated. It is easily soluble in 80% alcohol, sparingly in 90% alcohol. Analysis indicated $C_{24}H_{42}O_{21}=4(C_6H_{10}O_5)H_2O$. Mol. wt. found =595 (theory 666). It is said to give maltose and some "*iso*maltose" when saccharified by fresh malt extract at 45°C.

It is *identical* with the following:

F_1.—**Maltodextrin-β**, $[\alpha]_D$ 171·6°, $R_M=43\cdot0$ (Ling and Baker, J.C.S. 1897, **71**, 508), obtained by starch transformations using precipitated malt diastase at 70°C. (Action of Syniewski's β-diastase, Kuhn's α-diastase.) Formula: $C_{24}H_{42}O_{21}$. Mol. wt. found=670. It is incompletely converted by precipitated malt diastase in 24 hours. Product had $[\alpha]_D=140°$, $R_M=91\cdot5$.

F_2.—**Achroodextrin III**, $[\alpha]_D$ 171·1°, $R_M=42\cdot5$ (Prior and Wiegmann, Z. angew. Chem. 1900, **13**, 464) which is made by the incomplete conversion of potato starch paste by an extract of green malt (giving a red colour with iodine). Formula: $(C_{12}H_{22}O_{11})_2,H_2O$. It differs from Lintner and Düll's achroodextrin II in being partly fermentable by Saaz yeast and more fermentable by Frohberg yeast, by which *in vacuo* it is said to be completely fermentable. It is completely converted by Logos yeast. With diastase (½ hour at 50°, gradually rising to 60° and 70°C.) it gave maltose and Prior's achroodextrin IV, $C_{12}H_{20}O_{10},H_2O$, but no "*iso*maltose."

F_3.—"**Maltodextrin**," $[\alpha]_D$ 181·3°, $R_M=42\cdot5$ (Brown and Millar, J.C.S. 1899, **75**, 286), which was made by the action of kiln-dried malt (D.P. 38°L.) *i.e.* by the action of Syniewski's β-diastase, Kuhn's α-diastase *on highly concentrated starch solutions* (15%) at 55°C.

This has the same R_M as Ling and Baker's maltodextrin-β, but higher $[\alpha]_D$. It is said to give *maltose only* with fresh diastase, without the formation of "*iso*maltose" or stable dextrin. It is not in the slightest degree fermentable by (English) brewery yeast.

IV. The So-called "Stable Dextrins."

G.—**Stable-dextrin**, $[\alpha]_D$ 197–198°, $R_M=5\cdot5$ (Brown and Millar, J.C.S. 1899, **75**, 315), is made by the action of cold water extract of malt on gelatinised starch at temperatures below 60°C., the action being carried to the "resting stage" ($[\alpha]_D=150°$, $R_M=80$).

It is not resolvable by fractionation. Unlike the maltodextrins, it is attacked very slowly by large quantities of malt extract. A 7% solution was only saccharified to the extent of 30% after 48 hours by 25 c.c. of malt extract per 100 c.c. of solution. (The malt extract was prepared from a kiln-dried malt and found to be free from maltase.) The product consisted of equal parts of maltose and glucose. It was regarded as 39 $C_6H_{10}O_5$ groups and 1 $C_6H_{12}O_6$ (aldehydic). Mol. wt.=6,221.

H.—**Stable-dextrin**, $[\alpha]_D$ 185°, $R_M=14$ (Ling and Nanji, J.C.S. 1925, **127**, 636), which is made by the saccharification of potato starch by precipitated malt diastase (from brewer's malt Z.V. 30°) at 40°C. until the apparent maltose was 80·8%. The product was carefully fractionated. M.wt.=1,923. It is regarded as a *tetra-amylose* and said to be transformed slowly by maltase into *iso*maltose and with emulsin to give a mixture of maltose and glucose.

It is clearly quite a different material from Brown and Millar's stable dextrin.

Schardinger by the action of *Bacillus macerans* on starch obtained crystalline dextrins designated as α- and β- which Pringsheim has termed polyamyloses.

Pringsheim sets out the polyamyloses as

α-series.	Rotation.
α-hexa-amylose $[(C_6H_{10}O_5)_2]_3$	+139°
α-tetra-amylose $[(C_6H_{10}O_5)_2]_2$	+148·5°
di-amylose $(C_6H_{10}O_5)_2$	+136·5°
β-series.	
β-hexa-amylose $[(C_6H_{10}O_5)_3]_2$	+158°
Tri-amylose $(C_6H_{10}O_5)_3$	+151·5°

and describes their esters and halogen addition products.

Karrer and Bürklin (Helv. Chim. Acta, 1922, **5**, 181) question the existence of triamylose, and considers it and β-hexa-amylose to be a polymeride of maltose anhydride, *i.e.* an octa-amylose.

These polyamyloses yield glucose on complete hydrolysis, acetylbromide converts them into acetobromomaltose, whilst hydrochloric acid and silver carbonate cause the formation of amylobiose (*iso*maltose).

When tetra-amylose is dissolved in formamide and precipitated with alcohol, 80% of crystalline α-amylosan is obtained, and the balance of 20% is obtained as crystalline β-amylosan on distillation of the filtrate (Pringsheim, Wieder and Weidinger, Ber. 1930, **63**, [B], 2628).

The composition of these dextrins is as yet too uncertain to make further discussion of value. The subject has been discussed by Pringsheim ("Die Polysaccharide," Berlin, 1931; also "Chemistry of Monosaccharides and Polysaccharides," 1932, pp. 280–295), and by Pictet (X$^{\text{ème}}$ Conférence de l'Union Internationale de Chimie Liège, 1930).

The very properties which make the dextrins obscure chemically, namely, their varied properties, have been turned to advantage in industry, where they serve a wide variety of purposes as adhesives.

In industry the processes for the production of dextrin may be divided into two classes:

(1) Dry starch is subjected to the action of heat alone or with chemical agents.

(2) Wet starch, suspended in water or cooked to a jelly, is acted on with chemical agents with or without heat.

The former is the more important. The products vary greatly from almost pure white to dark brown, and there is no close definition of dextrin, though there is a U.S. Government specification. A summary of the subject with an abstract of the literature is given by Bloede in Walton's "Comprehensive Survey of Starch Chemistry," New York, 1928.

Any one of the starches in commerce can be used as raw material. Potato starch is the easiest to convert and produces the highest type of dextrin, but the taste developed makes it undesirable for postage stamps and envelope gum. Tapioca starch is preferable, producing tasteless products, and it is now the leading raw material for high-grade dextrin. Corn (maize) starches are inferior for many purposes, but as they are cheap they exceed all others in annual tonnage used.

The starch is first freed as much as possible from combined water by drying in suitable ovens, and then submitted to a temperature of 212–275° in rotating sheet-iron drums. The heat is supplied by hot oil, rape oil being fairly generally used, or by direct fire. When the oil-bath is used, the control over the temperature is greatest, and the colour of the product can be varied at will from white to dark brown. When the drums are heated by direct fire, they are made to rotate on slightly inclined axes, the dried starch being fed in at the higher end of the revolving cylinder and the product discharged at the other. Sheet-iron ovens are also used; they are constructed singly or in sets. The heat is supplied by a furnace, the heated air from which is drawn over the top of the ovens. The material is kept continually stirred by flat iron oars. Boxes and trays are also used as converters, and, indeed, the maker has only to consider the variety and quality of product required, and to remember that the drier the starch and the lower the temperature of conversion, the whiter will be the product, and, further, that different starches yield different products, *i.e.* behave differently when submitted to the action of heat, to enable him to construct an apparatus that will suit his requirements. It must also be borne in mind that the conversion takes place more slowly at a low temperature.

The alternative method, in which less heat is required to yield a satisfactory product, is to spray or moisten the starch either with a mixture of dilute nitric and hydrochloric acids, or with each acid singly, or with dilute oxalic acid. The paste is dried and heated at 100–120° or to 150°, till the transformation is complete, as determined by the iodine test; it must then be arrested promptly.

For a method of examination of commercial dextrin and related starch products, *v.* Babington, Tingle and Watson, J.S.C.I. 1918, **37**, 257T. The manufacture of potato dextrin is described by A. E. Williams (Chem. Trade J. 1932, **90**, 99; Ind. Chem. 1932, **8**, 114).

On heating dry starch with formic or acetic acids, the starch nucleus is broken down and esters of dextrins are formed, which are soluble in cold water. The proportion of acid fixed depends on the time of treatment. After 15 hours' heating with glacial acetic acid at 90°, the product just ceases to give a blue iodine coloration, and the products of the further heating are soluble in cold water. When care is taken to exclude moisture, and the heating is continued for 2 or 3 hours only, using equal weights of starch and glacial acetic acid, an acetylated starch, known commercially as *Feculose*, is obtained. This behaves like starch towards boiling water, but the jelly does not revert on standing. It forms very clear flexible films, and is said to give better results than dextrin as a textile finish (*see* Traquair, J.S.C.I. 1909, **28**, 288).

During hydrolysis the formation of glucose should be limited as far as possible, as it increases the hygroscopicity of the dextrin. The quantity present depends to some extent on the nature of the hydrolytic agent, of which $\frac{1}{2}$–$\frac{1}{30}$ of 1% is employed.

The operation of dextrinisation is said to be still largely an art, there being a variable resistance of the starch to the action of the hydrolysing agent, doubtless due to the presence of small but varying quantities of impurity in the starch. This view is supported by the fact that the resistance of the lower grades is more marked.

British gum differs from dextrin in having greater viscosity and producing a much thicker liquid when made up with the same quantity of water. This is due to the presence of only partly converted starch. For its manufacture roasting alone is generally sufficient, rapid heating to between 350° and 400°F. being essential.

"Gum powders" have recently become of importance as bottle adhesives and are special powdered forms of dextrin.

Paste or only partly converted dextrins are advantageously made by means of enzymes.

The thin boiling starches required by the textile industry are usually prepared by making a cream of the raw starch in water, adding the requisite amount of mineral acid, and digesting at 100–120°F., a temperature below the bursting point of the granules. A better, though more expensive, method is by treating the starch in the cold with an oxidising agent such as sodium hypochlorite.

Vegetable glue is prepared by alkaline treatment of starch, for example, by heating with 5% caustic soda with constant agitation to the bursting point of the starch granule. The stringy glue-like mass has high adhesive properties and is widely used in the wood-working industry as a substitute for animal glue.

E. F. A.

"DEVIL'S" DUNG *v.* Asafœtida.

DEXTROFORM. A non-poisonous combination of dextrin with formaldehyde which is used as a disinfectant dusting powder in the treatment of wounds and infected ulcers.

DEXTROSE, *glucose*, *v.* Carbohydrates.

DHAK GUM, a variety of Indian kino obtained from *Butea frondosa* Roxb. (*q.v.*).

DHURRIN is a cyanophoric glycoside isolated by Dunstan and Henry (Phil. Trans. 1902, **199**A, 399) from the leaves and stems of the great millet. It is *para*-hydroxymandelonitrile glucoside and is hydrolysed by emulsin.

E. F. A.

DIABASE. This name was introduced by the French mineralogist A. Brongniart, in 1807, for those varieties of basalt in which the light and dark minerals, respectively felspar and augite (or as he erroneously supposed, felspar and hornblende), are distinguishable to the unaided eye. As actually defined by him, the term is therefore synonymous with the *diorite* of Haüy (1822), whilst with the correction of augite for hornblende it becomes a synonym of the *dolerite* of Haüy (1822). In the latter sense it is used by some authors at the present time. Unfortunately, the term was re-defined by German petrographers, and it came to be applied to the older, or pre-Tertiary, dolerites, which differ from those of more recent date only in showing correspondingly more alteration, with the development of secondary minerals, such as *chlorite*. In consequence of this, the name "diabase" is now applied by most English authors to a partially altered or weathered dolerite. In this sense it has an economic bearing, since rocks of this class, being of wide distribution, are much quarried for road making. For this purpose the fresher dolerites are somewhat brittle, whilst diabases are tougher and more durable, providing that decomposition has not proceeded too far. There is also a tendency to use the name "diabase" in a loose sense, like the popular terms "greenstone," "whinstone," "toadstone," and "trap-rock."

L. J. S.

DIABETIN. Trade name for a preparation containing 12% of saccharine, 45% of sodium bicarbonate, 43% of tartaric acid and traces of red colouring material (J. Polak, Pharm. Weekblad, 1909, **46**, 519).

DIACETIN *v.* Acetin.

DIACETYL, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$, the first member of the aliphatic 1:2-diketones, a yellow liquid, b.p. 87–88°. The characteristic odour of butter is due to the presence of a small quantity of diacetyl (about 0·0005%) (*v.* Butter).

DIACETYLENES. The members of this group of hydrocarbons have two acetylenic linkages in the molecule. These linkages may be conjugated or unconjugated. Two principal classes of diacetylenes are to be recognised, *viz.* those in which the acetylenic linkages (one or both) are terminally situated and which consequently retain one or two reactive ("acetylenic") hydrogen atoms, and those in which all the reactive hydrogen atoms have been substituted by other groups. Substances of the former class (*e.g.* diacetylene) can display both substitutive and additive reactivity, whereas those of the latter class (*e.g.* dimethyldiacetylene) can only display additive reactivity.

Preparation.—Diacetylene, $CH\vdots C{\cdot}C\vdots CH$, is conveniently prepared by the action of cupric chloride solution on cuprous acetylide, followed by treatment of the copper diacetylide thus formed with dilute hydrochloric acid. The gaseous diacetylene so produced is purified in the Stock vacuum apparatus. Increase in the relative proportion of the cupric chloride, up to a point, increases the purity of the diacetylene produced, but also diminishes the total yield of gas owing to increased oxidation of the copper compounds (Straus and Kollek, Ber. 1926, **59**, [B], 1664). Diacetylene can also be prepared by the action of excess of alcoholic potassium hydroxide at 150–160° on butadiene tetrabromide (Lespieau and Prévost, Compt. rend 1925, **180**, 675), and it has been obtained together with numerous other products by maintaining an electric arc beneath the surface of ethyl alcohol (Müller, Helv. Chim. Acta, 1925, **8**, 826).

Symmetrically disubstituted diacetylenes of the conjugated type $R{\cdot}C\vdots C{\cdot}C\vdots CR$ can be smoothly prepared by the action of cupric chloride solution on the copper derivatives of monosubstituted acetylenes $RC\vdots CH$ (Straus and Kollek, *l.c.*), or by the action of iodine (2 atoms) on acetylenic Grignard reagents of the type $CR\vdots CMgX$ (Grignard and Tchéoufaki, Compt. rend. 1929, **188**, 357). Symmetrical diacetylenic hydrocarbons of unconjugated type are obtained (1) by the action of acetylenyl bromides on magnesium (sometimes sodium) in ether,

$$2CR\vdots C{\cdot}CH_2Br \xrightarrow{Mg} CR\vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}C\vdots CR,$$

(2) by the action of monosodio-acetylenes on polymethylene bromides,

$$2R{\cdot}CCNa + Br{\cdot}[CH_2]_5{\cdot}Br \longrightarrow R{\cdot}C\vdots C{\cdot}[CH_2]_5{\cdot}C\vdots CR,$$

and (3) by the action of suitable dibromo-olefins on polymethylene dibromides in presence of magnesium, followed by treatment of the product with alcoholic potassium hydroxide:

$$Br{\cdot}[CH_2]_7{\cdot}Br + 2CH_2{:}CBr{\cdot}CH_2Br \xrightarrow{Mg} CH_2{:}CBr{\cdot}[CH_2]_9{\cdot}CBr{:}CH_2 \xrightarrow{KOH} CH\vdots C{\cdot}[CH_2]_9{\cdot}C\vdots CH$$

From those diacetylenic hydrocarbons which contain one or two replaceable hydrogen atoms in the molecule, alkyl derivatives can be obtained by the action of methyl sulphate or other suitable alkylating agent (*see* Acetylenes) on a metallic derivative of the hydrocarbon:

$$[C\vdots C(CH_2)_2{\cdot}C\vdots C]Mg \xrightarrow{Me_2SO_4} CMe\vdots C{\cdot}(CH_2)_2{\cdot}C\vdots CH, \text{ and } CMe\vdots C{\cdot}(CH_2)_2{\cdot}C\vdots CMe$$

In general, unsymmetrical diacetylenic hydrocarbons can be obtained by the action of excess of hot alcoholic potassium hydroxide on the corresponding diolefin tetrabromides :

$$\mathrm{R{\cdot}CHBr{\cdot}CHBr{\cdot}[CH_2]_{\mathit{n}}{\cdot}CHBr{\cdot}CHBr{\cdot}R'} \xrightarrow{\mathrm{4KOH}} \mathrm{R{\cdot}C{\vdots}C{\cdot}[CH_2]_{\mathit{n}}{\cdot}C{\vdots}CR'}$$

Properties.—The diacetylenes are gases or liquids, usually of pronounced odour. Those compounds which retain one or two reactive hydrogen atoms in the molecule react with ammoniacal cuprous chloride, alcoholic silver nitrate, etc., to give metallic derivatives in the same manner as does acetylene, and with hypohalous acid (or under certain conditions with halogens) to give halogeno-acetylenes. Also all diacetylenes add chlorine, bromine, iodine, or hydrogen halide at their unsaturated centres.

Diacetylene, the simplest compound of the group, is a gas at room temperature (b.p. +9·5° to 10°/749 mm.; d_4^0 0·7364; $n_D^{0·8}$ 1·43862). It readily yields explosive metallic derivatives and in liquid form polymerises easily to give dark-coloured solid products; when heated, it forms liquid polymerides. By the action of iodine on the silver compound, or more conveniently, by the action of iodine and hypoiodous acid on the hydrocarbon, di-iododiacetylene is obtained; impure specimens of the latter are violently explosive. Di-iododiacetylene is transformed by iodine in ethereal solution to $\alpha\alpha\beta\gamma\delta\delta$-hexaiodobutadiene, m.p. 165·5–166·5°. With iodine in chloroform solution diacetylene yields the tetraiodide, $C_4H_2I_4$, m.p. 58–59°; with bromine it reacts with unexpected slowness, the main product being a hexabromide, m.p. 183·5°, but it gives also some proportion of an isomeric bromide, m.p. 114°. Diacetylene cannot be regenerated satisfactorily from the hexabromide by the action of zinc in an alcohol or acetone medium.

The conjugated diacetylenes can be hydrogenated catalytically and can evidently display some tendency towards terminal addition since diphenyl diacetylene on dihydrogenation undergoes 1:4-, 1:2:3:4-, and 1:1:4:4-addition simultaneously :

$$\mathrm{CPh{\vdots}C{\cdot}C{\vdots}CPh} \xrightarrow{\mathrm{H_2}} \begin{cases} \mathrm{CHPh{:}C{:}C{:}CHPh} \\ \mathrm{CHPh{:}CH{\cdot}CH{:}CHPh} \\ \mathrm{CH_2Ph{\cdot}C{\vdots}C{\cdot}CH_2Ph} \end{cases}$$

In general, each unsaturated centre of either conjugated or unconjugated diacetylenes is capable of displaying additive properties similar to those which characterise the simple acetylenes.

Conjugated Diacetylenes,

$\mathrm{R{\cdot}C{\vdots}C{\cdot}C{\vdots}CH}$ and $\mathrm{R{\cdot}C{\vdots}C{\cdot}C{\vdots}CR}$.

		B.p. (m.p.).
Methyl-diacetylene	($\Delta^{\alpha\gamma}$-Pentadi-inene)	42° (*c.*)
Ethyl- ,,	($\Delta^{\alpha\gamma}$-Hexadi-inene)	80° (*c.*)
n-Propyl- ,,	($\Delta^{\alpha\gamma}$-Heptadi-inene)	(?)
Dimethyl- ,,	($\Delta^{\beta\delta}$-Hexadi-inene)	130° (64°)
Diethyl- ,,	($\Delta^{\gamma\epsilon}$-Octadi-inene)	(?)
Di-*n*-propyl- ,,	($\Delta^{\delta\zeta}$-Decadi-inene)	88°/12 mm.
Di-*n*-butyl- ,,	($\Delta^{\epsilon\eta}$-Dodecadi-inene)	103°/8 mm.
Di-*n*-amyl- ,,	($\Delta^{\zeta\theta}$-Tetradecadi-inene)	118°–119°/4 mm.
Diphenyl- ,,	($\alpha\delta$-Diphenyl-$\Delta^{\alpha\gamma}$-butadi-inene)	(86·5–87°)
Dibenzyl- ,,	($\alpha\delta$-Diphenyl-$\Delta^{\beta\delta}$-hexadi-inene)	(101°)
Di-β-phenylethyl-diacetylene	($\alpha\theta$-Diphenyl-$\Delta^{\gamma\epsilon}$-octadi-inene)	(118°)

UNCONJUGATED DIACETYLENES.

	Formula.	B.p. (m.p.).	$d^{t°}$	$n_D^{t°}$
$\Delta^{\alpha\epsilon}$-Heptadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_2{\cdot}C{\vdots}CMe}$	26°–27°/3 mm.	0·810^{21}	1·4521^{21}
$\Delta^{\alpha\zeta}$- ,, ,,	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_3{\cdot}C{\vdots}CH}$	111·5°–112·5° mm.	0·8164^{17}	1·451^{17}
$\Delta^{\beta\zeta}$-Octadi-inene	$\mathrm{CMe{\vdots}C{\cdot}[CH_2]_2C{\vdots}CMe}$	62°/19 mm.	0·828^{30}	1·4658^{30}
$\Delta^{\alpha\theta}$-Nonadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_5{\cdot}C{\vdots}CH}$	55°–55·5°/13 mm. (−21°)	0·8159^{21}	1·452^{21}
$\Delta^{\alpha\kappa}$-Undecadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_7{\cdot}C{\vdots}CH}$	82·5°–83°/2 mm. (−17°)	0·8182^{21}	1·453^{21}
$\Delta^{\alpha\mu}$-Tridecadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_9{\cdot}C{\vdots}CH}$	(−3° to −2°)	0·8262^{21}	1·454^{21}
$\Delta^{\zeta\iota}$-Pentadecadi-inene	$\mathrm{C_5H_{11}{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}C_5H_{11}}$	134°–135°/4 mm.	—	—
$\Delta^{\alpha o}$-Hexadecadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_{12}{\cdot}C{\vdots}CH}$	152°–155°/12 mm.	—	—
$\Delta^{\zeta\iota}$- ,, ,,	$\mathrm{C_5H_{11}{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}C_5H_{11}}$	169°–170°/15 mm.	—	—
$\Delta^{\zeta\kappa}$,, ,,	$\mathrm{C_5H_{11}{\cdot}C{\vdots}C{\cdot}[CH_2]_2{\cdot}C{\vdots}C{\cdot}C_5H_{11}}$	157°–158°/10 mm.	—	—
$\Delta^{\eta\kappa}$-Heptadecadi-inene	$\mathrm{C_6H_{13}{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}C_6H_{13}}$	150°–155°/6 mm.	—	—
$\Delta^{\eta\lambda}$-Octadecadi-inene	$\mathrm{C_6H_{13}{\cdot}C{\vdots}C{\cdot}[CH_2]_2{\cdot}C{\vdots}C{\cdot}C_6H_{13}}$	167°–168°/7 mm.	—	—
$\Delta^{\alpha\tau}$-Eicosadi-inene	$\mathrm{CH{\vdots}C{\cdot}[CH_2]_{16}{\cdot}C{\vdots}CH}$	(54°)	—	—
$\Delta^{\kappa\nu}$-Tricosadi-inene	$\mathrm{C_9H_{19}{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}C_9H_{19}}$	(−12° to −10°)	—	—
$\Delta^{\kappa\xi}$-Tetracosadi-inene	$\mathrm{C_9H_{19}{\cdot}C{\vdots}C{\cdot}[CH_2]_2{\cdot}C{\vdots}C{\cdot}C_9H_{19}}$	(38·5°–39°)	—	—

E. H. F.

DIACRIDINES *v.* Acridine.

DIAL. 5:5-Diallylbarbituric acid, *Allobarbitone,* m.p. 171–172°. Hypnotic (*Ciba, London*), B.P.C. (*v.* Barbituric Acid).

DIALLAGE. An important rock-forming mineral belonging to the monoclinic series of the pyroxene group. It has the same composition as *diopside* and *hedenbergite,*

$$\mathrm{Ca(Mg,Fe)(SiO_3)_2},$$

but with the addition of alumina passes into *augite.* It differs from the other members of the pyroxene group in possessing a fine lamellar structure, due to secondary twinning and partial alteration of the material. On the surfaces of foliation the mineral displays a shining metallic sheen, and on this account it is sometimes used as an ornamental stone. The colour is grey, brown or green. Diallage is of common occurrence as a constituent of gabbro.

L. J. S.

DIALLYL, $\Delta^{\alpha\epsilon}$-*hexadiene* (*v.* Butadienes and Polyolefines (non-conjugated).

DIALURIC ACID, *Tartronylurea, v.* Barbituric Acid (Vol. I, p. 625*b*).

DIAMOND. Carbon crystallised in the cubic system. The contrast presented by the physical characters of the two forms of crystallised carbon—diamond and graphite—is very striking. Diamond is the hardest of minerals and, indeed, of all known substances, but at the same time it is very brittle; on the other hand, graphite is one of the softest of minerals, and it is flexible and inelastic. The one is colourless and transparent and a bad conductor of electricity, whilst the other is black and opaque and a good conductor. There is also a considerable difference in density—diamond, 3·52; graphite, 2·25.

The name diamond, in French and German *Diamant,* and similar in most other European languages, is a corruption of the Latin *Adamas,* which was used for this mineral by Manilius (A.D. 16) and Pliny (A.D. 100). This came from Ἀδάμας, meaning invincible, a word applied by the Greeks to hard metals and stones. The similar name adamantine-spar was used by the chemist Joseph Black for corundum. Although diamond and corundum are numbered respectively 10 and 9 in the mineralogist's scale of hardness, and with no other mineral falling between the two, yet, as shown by abrasive tests, diamond is 140 times harder than corundum, and more than a thousand times harder than quartz (No. 7 on the scale). It is on this high degree of hardness that all the technical applications of diamond depend; and a faceted gem never shows any signs of wear. The hardness is greater on an octahedron face than on a cube face, and on each face it varies with the crystallographic direction. Lapidaries assert that stones from Borneo and New South Wales are harder than those from other localities.

Crystalline Form.—Crystals of diamond are generally found singly and with faces developed on all sides; thus indicating that they grew freely from individual centres in some surrounding medium. By far the commonest form is the regular octahedron, the faces of which are often delicately marked with minute triangular pits or "etched figures," whilst the edges are nearly always rounded and often marked with a pronounced furrow. Other forms are a hexakis-octahedron (six-faced octahedron), and less often the rhombic-dodecahedron and the cube, while crystals of distinctly tetrahedral habit are rare. Nevertheless, it is probable that crystals of diamond are really hemihedral (tetrahedral-cubic); the apparent octahedron with grooved edges consisting of two tetrahedra interpenetrating in twinned position. Distinctly formed twinned crystals are not uncommon. These are contact-twins with a face of the octahedron as twin-plane, and the two individuals flattened parallel to this plane, giving a triangular plate with re-entrant angles at the three corners. These are known to the Dutch cutters as " naad-steenen " (suture-stones). In addition to the rounded edges, noted above, the faces themselves are often curved, sometimes to such an extent that the crystals are almost spherical in form. This rounding, as well as the etched figures, suggests that the crystals have been corroded subsequent to their growth. An important crystallographic character of diamond is the existence of perfect cleavages in four directions parallel to the faces of the octahedron. (On the crystallography of diamond, *v.* A. Fersmann and V. Goldschmidt, " Der Diamant," Heidelberg, 1911).

Physical Characters.—In its optical characters, diamond is remarkable for its very high refractive and dispersive powers, the indices being: for red light (B) 2·40735, yellow (D) 2·41734, violet (H) 2·46476, and the dispersive value (H–B) 0·05741. The critical angles of total reflection corresponding with these indices are 24° 33′, 24° 26′, and 23° 56′ respectively. The angles between the facets of the brilliant form of cutting adopted for the diamond are so arranged that a ray of light entering the gem by the front facet will meet the back facets at a greater angle than the critical angle, and will be internally totally reflected, passing out again from the front of the stone, and with a chance that rays of different colours will be separated. A cut stone, therefore, shows much brilliancy or " fire," together with flashes of prismatic colours. Corresponding with the high refractive index, diamond displays a high degree of lustre, which is of the quality known as " adamantine " lustre. Uncut stones, especially when not quite clear, and with rough rounded surfaces, present a peculiar and very characteristic lead-grey metallic appearance. When pure, diamond is without colour and perfectly transparent. The best stones are described as of the " first water " or " blue-whites." More often there is a tinge of colour (" off-coloured " stones), usually pale yellow, brownish, grey or greenish. Stones of a good canary-yellow, coffee-brown, or black colour are not uncommon, but those of rich shades of green, blue, or red are very rare. The nature of the colouring matter is uncertain, but it is probably inorganic (*e.g.* iron and titanium in the brown stones). Changes in colour may be effected by the action of heat or by exposure to radium emanations. Crystals of diamond, being cubic, should be optically isotropic, but when examined under the polarising microscope they are frequently seen to possess anomalous double refraction, especially around enclosures in the stone. This is due to a state of strain, but according to R. J. Sutton (1928) stories of exploding crystals are mythical. Luminescence (fluorescence and phosphorescence) is readily produced in some, but not all, diamonds by the action of sunlight, ultra-violet, Röntgen, cathode and radium rays, or simply by rubbing (triboluminescence). The cause of the luminescence was attributed by G. F. Kunz in 1895 to a hydrocarbon which he called "tiffanyite." Diamond becomes positively electrified by friction. It is very transparent to the Röntgen rays; whilst glass imitations are opaque. Being a good conductor of heat, it can be distinguished from a glass imitation by touching with the tip of the tongue, diamond feeling much colder than glass; also a film of moisture from the breath will disappear more quickly off the surface of diamond than off glass. The specific heat is less than that of graphite, and it increases rapidly with the temperature. Colourless diamonds (apart from those that are distinctly coloured) show amongst themselves differences in the absorption bands in the infra-red and the ultra-violet; and some of them develop an electric current when exposed to ultra-violet light—photoelectric effect (R. Robertson, J. J. Fox and A. E. Martin, Phil. Trans. 1934, 232A, 463).

Chemical Characters.—The combustibility of diamond was first proved experimentally by the Florentine Academicians in 1694. Lavoisier, in 1772, found that the presence of air was necessary, and that " fixed air " resulted ; but it was Smithson Tennant, in 1797, who first proved that equal weights of diamond and carbon yielded equal weights of carbon dioxide. More convincing experiments in this direction have been made by Davy, Dumas and Stas, A. Krause (1890) and H. Moissan (1893). Powdered diamond burns readily in air at a red heat. Moissan determined the temperature of ignition in oxygen to be 690–790° ; according to J. Joly it is 850° in air. It burns with a small pale-blue flame, and in oxygen is able to support its own combustion. It is infusible even in the electric arc ; and it can be heated at high temperatures (1,500°) without alteration in various gases (hydrogen, nitrogen, sulphur dioxide and trioxide, and nitrous oxide). In carbon dioxide, however, at 1,200° the crystals are corroded, with formation of carbon monoxide. It is unattacked by acids, caustic alkalis, iodic anhydride, hydrogen potassium sulphate, or a mixture of sodium chlorate and nitric acid, but is oxidised when heated to 180–230° in a mixture of potassium dichromate and sulphuric acid. In fused potassium nitrate or sodium carbonate at about 900° small etched figures are slowly produced ; at 1,200° the action is more rapid, carbon dioxide being liberated. It is acted upon by sulphur vapour at 900° ; and it combines with iron, yielding steel. Crystals are etched by molten olivine (magnesium silicate). The fact that diamond gives with oxidising agents only carbon dioxide, whilst graphite yields graphitic oxide, has led to the suggestion that these two forms of carbon are chemical isomerides. Observations at high temperatures are somewhat contradictory ; a mere blackening of the surface has often been observed, but not always confirmed. C. Doelter (1911), with crystals packed in charcoal or thorium oxide and heated to 2,500°, obtained only a superficial blackening without any alteration in the physical characters of the material. Moissan (1893), however, records the conversion into graphite at the temperature of the electric arc (about 3,600°); and Parsons and Swinton (1907) found that a diamond placed in the focus of cathode rays *in vacuo* swelled up into a coke-like mass when the temperature reached 1,890°. In this connection the occurrence of cubes of graphite (*cliftonite*) in meteoric irons is significant; these are supposed to be paramorphs after diamond.

The ash remaining when diamond is burnt amounts, for colourless crystals, to 0·02–0·05%, but in the less pure carbonado it may reach 4·8%. It consists mainly of iron oxide and silica, with some lime, magnesia, and titanium. The iron and titanium may represent the colouring matter present in the stone ; but the frequent presence of minute enclosures in diamond is not to be overlooked. In addition to liquid enclosures (carbon dioxide and water), the following materials have been recorded: black carbonaceous matter, magnetite, ilmenite or hæmatite, quartz, rutile, pyrite, gold, garnet, olivine, chlorite (?), apophyllite, etc. (R. J. Sutton, Min. Mag. 1921, **19**, 208; L. J. Spencer, *ibid.* 1924. **20**, 245).

Varieties.—Differing in certain points from the general characters enumerated above, there are two varieties of diamond—bort and carbonado—which, for technical purposes, are more important than the purer crystals used for gems. These are crystalline aggregates, as distinct from single well-developed crystals.

Bort (boart or boort) consists of a number of individual crystals with a radial grouping around a common centre, giving rise to rounded exterior forms. These are sometimes quite spherical (" shot-bort " or " ballas "). They are usually rough on the exterior, it being only here that the fibres, or individual crystals, have been free to develop crystal faces—in the interior these have interfered with each other's growth. Although each individual possesses the cleavage characteristic of diamond, yet for the whole mass there is no continuous cleavage. For this reason, bort is tougher than the single crystals, which readily split along the cleavage directions, and is thus better adapted for boring, turning and cutting tools. This, no doubt, is the explanation of the common statement that bort is harder than diamond ; further, since in crystals the degree of hardness varies with the direction, a chance section of bort will present both maximum and minimum values. The rounded pieces of bort are translucent to cloudy and opaque. They are grey or black with a greasy to metallic lustre, and, usually, a peculiar leaden appearance ; sp.gr. 3·50. In the trade the term bort also includes fragments (such as those obtained by bruting), and all crystals and stones that are useless for gem purposes. Such material is of value as an abrasive.

Carbonado, or " black diamond " (known in the trade as " carbon " or " carbonate "), is a finely granular crystalline material, dull, black and opaque, and often more or less porous, with somewhat the appearance of coke. It forms irregularly shaped masses, and consists of a confused aggregate of minute crystal grains of diamond. It therefore presents no cleavage as a whole, and is consequently tougher and less frangible than single crystals. It is less pure than ordinary diamond, yielding more ash (up to 4·8%) when burnt. An analysis of the ash gave Fe_2O_3 53·3%, SiO_2 33·1%, CaO 13·2%; MgO trace. The sp.gr. is less, 3·15–3·34 (the value for crystals being between the limits 3·502–3·525). The largest known piece of carbonado was found in Bahia, Brazil, in 1895. It weighed 631·9 g., that is, slightly more than the famous " Cullinan " diamond (which weighed 621·2 g.). Both carbonado and bort show considerable variations in texture, and with increasing coarseness of grain they may pass insensibly into ordinary diamond.

Occurrence.—*India*, from very remote times until the middle of the eighteenth century, was the only source of diamond (with the unimportant exception of Borneo). Since the discovery of the Brazilian and South African deposits the output has gradually fallen off, the fluctuating annual output being returned as only 20 carats in 1916 and 2,480 carats in 1934. The secondary deposits have, however, only been worked by native methods, and the original deposits have not been discovered. Indian diamonds being of the best gem-quality, there is thus a possibility of further developments. They occur associated with pebbles of jasper and vein-quartz in thin beds of conglomerate in the ancient sedimentary rocks (sandstones and shales) of the Vindhyan system (of pre-Cambrian age), which rest directly on the crystalline rocks. With the weathering of these strata, the diamonds are accumulated in the alluvial deposits of the present rivers. The districts where mining has been done fall into three main groups : a southern group in the basins of the Pennar, Kistna and Godavari rivers in Hyderabad and Madras; an eastern group in the Mahandi and Brahmani valleys in Bihar and Orissa ; and a northern group between the Ken and Son rivers near Panna in Bundelkhand. A doubtful occurrence of diamond in pegmatite has been described from Wajra Karur near Bellary; and, unfortunately, nothing is known as to whence the diamonds found in the ancient sedimentary rocks were derived. (On Indian diamonds, *v.* Manual of the Geol. of India, vol. 3, Economic Geology, 1881, by V. Ball ; vol. 4, Mineralogy, 1887, by F. R. Mallet ; J. C. Brown, " India's Mineral Wealth," 1936).

In *Brazil*, diamonds were discovered about 1725 in the alluvial gold-washings at Tejuco (now Diamantina) in Minas Geraes; and, although they have been since found in several other districts, notably in Bahia, this has remained the principal diamond-mining centre. Here, as in India, the diamond-bearing alluvial deposits have been derived from conglomerates and sandstones (including the flexible sandstone known as itacolumite) of considerable geological age (pre-Cambrian), and the original rock from which these were derived is not known. The Brazilian deposits are, however, remarkable for the variety of minerals found as well-worn pebbles (" favas ") in association with the diamond ; and the nature of these minerals, or indicators, has led to the suggestion that they, together with the diamonds, originally came from quartz-veins. (On Brazilian diamonds, *see* E. Hussak, " Os Satellites do Diamante," Rio de Janeiro, 1917; H. Preston, J. Soc. Arts, 1909, **58**, 101; L. J. Moraes and D. Guimarães, Ann. Acad. Brasil. Sci. 1930, **2**, 153, and Econ. Geol. 1931, **26**, 502; C. W. Correns, Z. pr. Geol. 1932, **40**, 161, 177).

In *South Africa*, diamonds were first discovered in 1867 near Hopetown on the Orange River. In 1868 the important workings (" river diggings ") on the Vaal River were commenced; and in 1870–1871 the diamonds were traced to deposits of a unique type, in the neighbourhood of which the town of Kimberley in Griqualand West, Cape Province, very quickly sprang up. Here are situated the famous mines De Beers, Kimberley, Dutoitspan, Bultfontein and Wesselton. Other mines of the same type are the Jagersfontein and Koffyfontein mines in Orange Free State, and the great Premier mine (discovered in 1902) near Pretoria in the Transvaal. The diamond-bearing rock of these mines fills volcanic pipes, 200–300 yards (in the case of the Premier mine half a mile) across, penetrating vertically the surrounding beds of basalt, shale diabase, and quartzite, and extending to unknown depths. The rock, known as *kimberlite* or locally as " blue ground," consists mainly of a hydrated magnesium silicate with much the same composition as serpentine. It contains boulders and broken fragments of various rocks (basalt, shale, sandstone, quartzite, granite, mica-schist, eclogite, etc.) and minerals (ilmenite, pyrope, enstatite, chrome-diposide, pyrite, etc.) and is of the nature of a volcanic agglomerate. Diamond is present in this rock on an average of one part in fourteen millions (0·00008%), and in the richest part of the Kimberley mine one part in two millions. The diamond was brought up from below with the igneous material, which must have been derived from a basic magma rich in olivine. Although the origin of diamond has been the subject of much discussion, there seems no reason to doubt but that it crystallised from this basic magma. The rare presence of diamonds embedded in boulders of *eclogite* (a garnet-pyroxene rock) found in the blue ground has led to the suggestion that this is the mother-rock ; but it is quite conceivable that the mineral crystallised from more than one kind of basic magma.

The early open workings (" dry diggings ") at the Kimberley mines were soon replaced by a regular system of underground mining. The hard blue ground, when brought to the surface, was formerly spread out on extensive floors and exposed to the action of the weather for about a year, when it is crumbly enough to enable the heavy minerals to be separated by washing. The present method is to pass the rock directly through crushers and rollers. From the concentrate the diamonds are separated by means of a mechanical sorting table coated with grease, to which the diamonds adhere, whilst the other minerals pass over. Finally, the stones are cleaned by boiling in a solution of caustic soda and in aqua regia or hydrofluoric acid.

Many kimberlite pipes are found over a wide area in South Africa, some extending also into South-West Africa, Southern Rhodesia, Belgian Congo and Tanganyika Territory; but only a few of them have proved to be productive. These pipes, of Cretaceous age, have no doubt supplied the diamonds found in the sand-dunes in South-West Africa, and the rich deposits found in 1927 and 1929 along the coast respectively south and north of the mouth of the Orange River. Rich alluvial deposits were discovered in 1926 in the Lichtenburg district in south-western Transvaal, where the gravels of an ancient river system are richest in diamonds in large pot-holes in the underlying dolomite-rock. It is possible, however, that some of these alluvial diamonds may have been derived from rocks of much greater geological age, for small green diamonds are occasionally found in the gold-bearing conglomerate ("banket") at Modderfontein in the eastern Witwatersrand. In these rocks, of pre-Cambrian age, the diamond must have come from some earlier source, of which no trace has yet been found. (On South African diamonds, *see* G. F. Williams, "The Diamond Mines of South Africa," 2nd ed., New York, 1907; P. A. Wagner, "The Diamond Fields of Southern Africa," Johannesburg, 1914; J. R Sutton, "Diamond—A Descriptive Treatise," London, 1928; A. F. Williams, "The Genesis of the Diamond," 2 vols., London, 1932).

Since 1903 diamonds have been discovered in several other parts of Africa. They have been found in conglomerates of Triassic age near the borders of Belgian Congo and Portuguese Angola and extending northwards into French Equatorial Africa (E. Polinard, Ann. Soc. Géol. Belg. Publ. Congo Belge, 1929, **52**, C179; 1934, **57**, C65; Bull. Acad. Roy. Belg. 1931, **17**, 137). In West Africa many small diamonds are found in alluvial deposits in the Gold Coast, a few in Liberia and Sierra Leone, and in 1934 a single fine crystal of 10 carats in Northern Nigeria. In Tanganyika Territory a large kimberlite pipe and the overlying gravel have been worked since 1921 at Mabuki, 35 miles S.S.E. of Mwanza on the south shore of Lake Victoria. Several kimberlite pipes were found in 1926 farther south near Shinyanga. Diamond is also reported from Bagamoyo on the east coast opposite Zanzibar (E. O. Teale, Geol. Survey Tanganyika Territory, 1931, Short Paper No. 9).

Other diamond-producing countries of less importance are British Guiana, Borneo, and New South Wales. In the interior of British Guiana many small diamonds are found together with gold in alluvial deposits along the Mazaruni and Potaro rivers. Finds of isolated crystals have been reported from Russian Lapland, Ural Mountains, Bohemia, China, Western Australia, British Colombia, Venezuela, etc. In the northern portion of the United States single crystals are occasionally found in glacial deposits, which have no doubt been derived from some unknown source in Canada. At Murfreesboro in Arkansas some diamonds have been found in a serpentinised peridotite rock allied to kimberlite (H. D. Miser and C. S. Ross, Econ. Geol. 1922, **17**, 662).

The *production* of diamond was at one time practically a monopoly of South Africa, and by limiting the output and holding large stocks in reserve, prices have been artificially kept high. But now there are several competitors in other regions, though South Africa still accounts for more than half the world's total production. In the following table is given the output for the best and worst years since 1914. The total output in 1928 of 7,742,000 metric carats is equivalent to 1548·2 kg. or rather over 1½ metric or long tons (5 metric carats=1 g.), valued at £20,200,000. In 1936 and 1937 the production reached eight and nine million carats respectively, more than half in each year coming from Belgian Congo.

DIAMOND PRODUCTION OF THE WORLD
(in metric carats).

	1914	1922	1928
Union of South Africa :—			
Mines . . .	2,727,558	465,634	2,254,649
Alluvial . .	147,742	203,925	2,114,675
South-West Africa	*	114,156	503,142
Belgian Congo .	23,877	250,292	1,647,700
Angola . . .	—	98,683	237,511
Gold Coast . .	—	6,535	698,826
Southern Rhodesia	1,005	256	54
Tanganyika Territory. . . .	—	—	24,681
Brazil	*	*	41,865
British Guiana .	13,716	163,640	214,474
Borneo . . .	*	1,948	667
India	55	171	824
Australia . . .	1,580	1,000	28
Total . .	2,916,000	1,337,000	7,742,000

* Figures not available.

The presence of diamond in certain *meteorites* is of special interest. It was first observed in the stone which fell on September 4, 1886, near the village of Novo-Urei, Nizhni Novgorod, Russia. This stone is composed of olivine (67·5%) and augite (23·8%), together with nickel-iron, troilite, chromite, black carbonaceous matter, and about 1% of diamond, the last as minute greyish grains. As dull black grains it has also been found in the meteoric stone of Carcote, Chili. In several, though not in all, of the masses of meteoric iron from Cañon Diablo in Arizona it has been found as colourless crystals, and as black and colourless grains, the largest 1 mm. across. It is also recorded from the meteoric iron of Magura, Czechoslovakia. The cubic form of graphite (cliftonite), probably a pseudomorph after diamond, has been found in the meteoric irons of Youndegin (Western Australia), Smithville (Tennessee), Crosby's Creek (Tennessee), and Magura (Czechoslovakia).

Origin and Artificial Production.—The reported occurrences of diamond in acid igneous rocks and in quartz-veins are very doubtful. On the other hand, its presence in basic igneous rocks is well established; *e.g.* in kimberlite and eclogite in South Africa, in serpentinised peridotite in Arkansas, and in diabase in New South Wales; whilst in meteoric stones the matrix is also of the same general character. In these cases the diamond is very probably present as a primary mineral, and one of the first constituents to crystallise out from the basic silicate magma. In addition, we have the occurrence of diamond in the nickel-iron of meteorites. This may be regarded as a magma of a still more basic type, and it is thus probable that diamond may crystallise from basic magmas of widely varying composition.

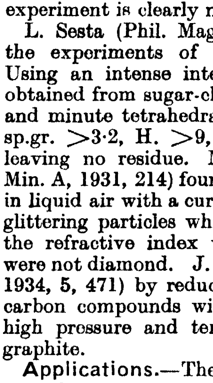
Many attempts have naturally been made to constrain the abundant element carbon to crystallise as the rare and valuable diamond. Considerable doubts have recently been expressed as to whether diamond has ever been produced artificially (C. H. Desch, Nature, 1928, **121**, 799; F. Krauss, "Synthetische Edelsteine," Berlin, 1929; F. Stöber, Chem. Erde, 1931, **6**, 440; R. Brauns, Zentr. Min. A., 1931, 218; M. K. Hoffmann, Fortschr. Min. Krist. Petr. 1933, **18**, 17). The alleged products have never been more than the minutest particles, and these have not been subjected to rigorous tests. The hardness test by scratching has been mainly relied on; but many carbides have a high degree of hardness, and spinel, which may crystallise as colourless octahedra, readily scratches quartz. The appearance under the microscope alone is not reliable, and no definite determinations appear to have been made of the refractive index, specific gravity, or X-ray diffraction patterns.

The experiments of I. Friedländer (1898), and of R. von Hasslinger (1902–1903), in which carbon was dissolved in molten magnesium silicate (olivine or kimberlite), bear some relation to the natural occurrences, but doubts have been expressed as to whether the microscopic crystals so obtained were really diamond. A method often tried is that first used by R. S. Marsden (Proc. Roy. Soc. Edin. 1881, **11**, 20) and elaborated by Moissan (1893–1896; "Le Four électrique," Paris, 1897; and "The Electric Furnace," London, 1904), in which carbon is dissolved in silver or iron at a high temperature and the mass suddenly cooled by immersion in water or lead. A contracting crust is so formed and the molten interior subjected to great pressure. Sir C. A. Parsons (Bakerian Lecture, Phil. Trans. 1919, A., **220**, 67; J. Inst. Metals, 1918, **20**, 5), from a long series of experiments, however, concludes that pressure is not a necessary condition, and that the diamond had been formed from gases, probably carbon monoxide, occluded in the iron. E. de Boismenn ("Fabrication synthétique du Diamant," Paris, 1913) states that he obtained crystals up to 2 mm. across by the electrolysis of fused calcium carbide. O. Ruff (Z. anorg. Chem. 1917, **99**, 73), in a systematic repetition of the various methods, obtained negative results, except perhaps by Moissan's method.

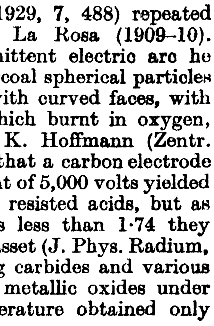
L. Duparc and P. Kovaleff (Compt. rend. Soc. Phys. Nat. Hist. Genève, 1924, **41**, 108), from a consideration of the equilibrium relations of diamond and graphite, conclude that the stability of diamond increases with pressure and diminishes with temperature, and an attempt was made to produce diamond at ordinary temperature under very high pressure, as in Spring's experiments. Carbon disulphide and a metal with a strong affinity for sulphur were subjected to a pressure of 8,000 atm. Dissolving the metal in acid, there remained a minute residue of colourless irregular grains which were birefringent with high refraction and which readily scratched glass. After some days the particles became covered with an opaque crust and fell to a fine powder. The suggestion that diamond was formed in this experiment is clearly not substantiated.

L. Sesta (Phil. Mag. 1929, **7**, 488) repeated the experiments of M. La Rosa (1909–10). Using an intense intermittent electric arc he obtained from sugar-charcoal spherical particles and minute tetrahedra with curved faces, with sp.gr. $>3{\cdot}2$, H. >9, which burnt in oxygen, leaving no residue. M. K. Hoffmann (Zentr. Min. A, 1931, 214) found that a carbon electrode in liquid air with a current of 5,000 volts yielded glittering particles which resisted acids, but as the refractive index was less than 1·74 they were not diamond. J. Basset (J. Phys. Radium, 1934, **5**, 471) by reducing carbides and various carbon compounds with metallic oxides under high pressure and temperature obtained only graphite.

Applications.—The value of diamond as a gem depends on its high degree of hardness enabling it to resist wear, and its high refractive and dispersive powers. These optical characters are, however, only brought into full play when the stone is faceted in a particular manner; and for this reason, old stones cut by Indian lapidaries have often been re-cut. The form most suited for this purpose is the brilliant-cut, and stones so cut are known as brilliants. The rose-cut, or rosette, is only used for quite small stones usually mounted in number as a surround. The accompanying figures show a brilliant viewed on the large front facet, or table, and a side-view; and the rose-cut, viewed from above and the side. Being the hardest known material, diamond can only be worked very slowly and tediously with its own powder. The groundform of the brilliant is approximately an octahedron, and this can be obtained, if necessary, by cleavage, or more safely by the modern



Brilliant-cut.



Rose-cut.

method of sawing with a thin metal disc charged with diamond dust. The brilliant is then roughly shaped out by rubbing two diamonds together—a process known as *bruting.* The final grinding and polishing of the facets are performed on a rapidly revolving cast-iron disc fed with diamond dust and olive-oil.

The large historical diamonds with their associations of mystery and romance are mostly of Indian origin ; but these are now eclipsed by the numerous much larger stones found in South Africa. The largest Indian stone still preserved is the " Koh-i-noor," which was re-cut in England in 1852 as a brilliant of 106$\frac{1}{16}$ carats[1] (=21·786 g.). The largest Brazilian stone, the " Star of the South," found in 1853, weighed in the rough 254½ " carats," and when cut 125 " carats." The largest known crystal of diamond is the " Cullinan," which was found in 1905 in the Premier mine, Transvaal. This showed a large cleavage surface, and was only a portion, probably about half, of the complete crystal. The portion as found weighed 621·2 g. (3,106 metric carats, or nearly 1 lb. 6 ozs. avoirdupois). Being too large to cut as a single stone, it was cleaved and cut as nine large gems (weighing from 104·06 to 0·88 g.) and ninety-six small brilliants, the yield of cut material amounting to 34½%. The " Cullinan," although the largest crystal, is not the largest piece of diamond that has hitherto been discovered. A mass of carbonado weighing 631·9 g. was found in 1895 in Bahia, Brazil.

As an abrasive, diamond powder is the most effective agent available. It is the only material with which diamond itself can be worked, and it is much used by lapidaries for cutting other hard stones. A thin disc of soft iron charged on the edge with diamond powder is used for sawing stones, both for ornamental purposes and in the preparation of thin microscope sections of rocks. The small steel tools used by engravers of cameos and intaglios, and also the steel points used for boring precious stones, etc., are charged with diamond dust. The material used for abrasive purposes, though included in the trade under the term *bort,* consists of the waste material from shaping the better stones as brilliants, and also the less clear and spotted crystals not suitable for cutting as gems. It is crushed in a diamond-mortar, splinters suitable for other purposes being picked out under a magnifying glass, and the remainder reduced to a fine powder.

The glazier's diamond is a crystal or fragment bounded by two rounded crystal-faces meeting in a curved or cusped cutting edge. For writing, drawing and engraving (*e.g.* fine scales and rulings on glass, metal, stones, ivory, etc.) fine splinters are used, or the diamond may be cut to a rounded point or chisel-edge. Diamond points are also used for drilling hard stones, glass, porcelain, teeth, etc.

Carbonado and bort, by reason of their absence of cleavage, are much more suitable than ordinary diamond for mounting as small fragments (2–3 carats in weight) as cutting tools which may be subjected to shocks. These are mounted in the crowns of rock-drills, used in tunnelling, mining, and sinking bore-holes for artesian wells, etc. ; and on the edges of blade, band, circular, or wire saws for sawing large blocks of marble, granite, etc. Fragments, either in a rough form or fashioned to a suitable shape, are mounted as lathe tools for working stone, metal, etc. For example, for turning electric-light carbons, the edges of watch-glasses, finishing accurate turning work of the hard steel axles of instruments and machines of precision, boring cannon, forming the sharp-edged furrows on the grinding surfaces of millstones, for dressing emery wheels, etc.

Small cleavage plates or flat crystals of diamond drilled from each side with fine conical holes are used for drawing fine wire, down to 0·01 mm. in diameter. For the tantalum, tungsten and osmium filaments of electric lamps the metal is forced by pressure through the hole. Bored diamonds are also used for the pivot-supports of delicate instruments, such as chronometers, electric meters, etc.

The application of diamond for optical purposes is limited by the high cost and difficulty of working. Diamond lenses would need to have a much slighter curvature than those of glass, and they would be immune from scratching. Microscope objectives with such lenses were constructed by Pritchard under the direction of C. R. Goring, in 1824–1826. A hemisphere of diamond would also increase considerably the range and durability of refractometers.

References.—In addition to the references quoted in the several sections above, the following are given as being of a more general character: M. Bauer, " Edelsteinkunde," Leipzig, 1896—3rd ed. by K. Schlossmacher, Leipzig, 1928–32—Eng. transl. (" Precious Stones "), by L. J. Spencer, London, 1904; C. Hintze, " Handbuch der Mineralogie," Leipzig, 1898, vol. i.; C. Doelter, " Handbuch der Mineralchemie," Dresden and Leipzig, 1912, vol. i.; Sir W. Crookes, " Diamonds," London, 1909; Sir H. A. Miers, " Diamond," article in Encycl. Brit. 11th ed., 1910; E. Boutan, " Le Diamant," Paris, 1886; E. W. Streeter, " The Great Diamonds of the World," London, 1882; W. R. Cattelle, " The Diamond," London, 1911 ; P. Grodzinski, " Diamant-Werkzeuge : Darstellung der Anwendung des Diamanten in Industrie und Gewerbe," Berlin, 1936.

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***o*-DIANISIDINE,** 4:4′-diamino-3:3′-dimethoxydiphenyl, colourless crystals, m.p. 135°, used as an intermediate for direct cotton dyes.

DIARSENOL. Canadian arsenical of the salvarsan type (J. Messner, Z. angew. Chem. 1917, **30**, 49; Pharm. Monatsh. 1921, **2**, 19).

DIASPIRIN. Trade name for the substance called succinyldisalicylic acid (G.P. 196634) probably identical with the salicylyl succinide ether-ester of H. P. Kaufmann (Z. angew. Chem. 1927, **40**, 69) ; m.p. 178°, antipyretic.

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[1] This was the old English carat of 205·409 mg. A later value of the English carat, as defined by the Board of Trade in 1888 and 1889, was 205·304 mg. The carat-weight has now been standardised in all countries as the *metric carat* of 200 mg. (5 carats = 1 g.). This has been the legal value of the carat in the British Isles since April 1, 1914.

DIASPORE. A native hydrated alumina, $Al_2O_3{\cdot}H_2O$ or $AlO(OH)$, crystallising in the orthorhombic system and isomorphous with goethite and manganite. It is usually found as scales or foliated masses with a perfect cleavage in one direction on which the lustre is pearly; but it is readily distinguished from other foliated minerals (mica, etc.) by its much greater hardness (H. 6½–7). Sp.gr. 3·4. When heated before the blowpipe it decrepitates violently, breaking up into pearly white scales (hence the name diaspore, from διασπείρειν, to scatter). In colour, it is usually grey or yellowish-brown, but pale-violet crystals are also found. It is usually found as an alteration product of corundum and emery, but occurs also as a mineral of contact-metamorphic origin in crystalline limestones. It is of importance as a constituent of bauxite, and in a particular type of bauxite, called *diasporite*, occurring in crystalline limestone in the Bihar Mountains, Hungary, it constitutes the bulk of the material.

L. J. S.

DIASPORITE *v.* DIASPORE.

DIASTASE *v.* AMYLASE and BREWING.

DIATOMITE (*Diatomaceous Earth, Infusorial Earth, Tripolite* or *Tripoli*; Ger. *Kieselguhr, Bergmehl*). A form of opaline silica consisting of the siliceous remains of diatoms (Diatomaceæ). These are unicellular, free-swimming plants belonging to the large group of Algæ. The cell-wall, or frustule, of each minute individual consists of two shields or valves of siliceous material with elaborate and beautiful ornamentation. More than 10,000 species of diatoms have been described; they vary considerably in form—fusiform, elliptical, discoidal, globular and acicular. Material composed of individuals of the acicular form, the length of which varies from 0·093 to 0·156 mm. and the thickness 0·00156–0·00468 mm., is best suited for technical purposes. Diatoms multiply extremely rapidly and inhabit both fresh and salt water, being more abundant in cold latitudes. On death, their remains accumulate, under certain conditions, at the bottom of swamps, lakes or the open ocean. Besides being formed at the present day, such deposits are also met with in strata of Pleistocene and Tertiary age.

Diatomite is a loose, pulverulent material with a mealy or earthy texture, resembling soft chalk or dried clay in appearance. It is friable between the fingers with a harsh feel, and grates between the teeth. In colour it is white, grey, yellowish, brownish or greenish. It is very light, floating on water; sp.gr. of air-dried material 0·24 and of calcined 0·34. Its high degree of porosity depends on the fact that the shells of the diatoms are hollow. Good material absorbs four or five times its weight of water. Further, it is a bad conductor of heat, electricity and sound, and is resistant to heat and most chemicals. Of acids, only hydrofluoric attacks it, but it is slowly dissolved by a hot solution of caustic alkali. Chemically it consists of hydrated silica, mixed with various impurities, such as sand, hydroxides of iron, clayey, calcareous and organic matter. 70–90% of SiO_2 may be present.

Analysis I is of white material (dried at 105°) from Auxillac, Cantal, Auvergne; II, of green material from Auxillac; III, from Loch Cuithir (or Quire), Skye, Scotland; IV, from Richmond, Virginia; and V. of tripolite from Bilin, Bohemia (including also SO_3 0·12, P_2O_5 0·24, NH_4 0·03).

	I.	II.	III.	IV.	V.
	%	%	%	%	%
SiO_2 .	91·61	88·56	88·73	75·86	74·20
TiO_2 .	0·10	0·18	—	—	—
Al_2O_3 .	1·53	2·16	—	9·88	6·81
Fe_2O_3 .	2·22	0·73	0·67	2·92	
CaO .	0·18	0·26	0·04	0·29	0·41
MgO .	0·29	0·02	—	1·63	—
K_2O .	trace	0·47	—		0·02
Na_2O .	trace	0·44	—		0·30
H_2O .	2·33	3·01	6·40	8·37	13·30
Organic matter	1·74	4·17	4·15	—	4·20

Tripolite (Ger. *Tripel*, *Polierschiefer*=polishing shale) differs from diatomite in being more compact with a laminated structure and consequently less light (sp.gr. 1·86) and porous. It merely represents the same material of a greater geological (Tertiary) age.

The most extensively worked deposits of typical diatomite (Kieselguhr) are those on the Lüneburger Heide (heath) in Hanover. Here beds with a thickness of 10–15 m. occur in basins in Pleistocene sands. The uppermost layers are white, below they are grey, and at the bottom of the deposit green. The green material contains from 15 to 30% of organic matter, sufficient for calcination without addition of fuel. A bed of 5–7 m. covered by Tertiary clay and basalt is worked at Vogelsberg near Altenschlirf in Hesse. Similar deposits of recent to Miocene age are also widely distributed in the volcanic region of central France (Departments of Cantal and Puy-de-Dôme). Here the material is known as *randannite* and *ceyssatite*, from Randanne and Ceyssat respectively; and it is worked commercially under the name *tellurine*. (On the French and German deposits, *see* C. Schmidt, Ann. des Mines, Paris, 1910, **17**, 370). Deposits are met with in peat-bogs at several places in Scotland, and beds up to 40 ft. in thickness of good quality material are worked at Loch Cuithir (or Quire) in the parish of Kilmuir in Skye (W. I. Macadam, Min. Mag. 1884, **6**, 87; 1886, **7**, 30, 35; 1889, **8**, 135. Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1916, **5**). Similar deposits also occur in Co. Antrim (J. H. Pollok, Sci. Proc. Roy. Dublin Soc. 1899, **9**, 33). Extensive deposits, many of them of Tertiary age, are of wide distribution in the United States, especially in California (H. Ries, "Economic Geology," 6th ed., New York, 1930). Other localities are Monte Amiata in Tuscany, Victoria, Norway, Denmark, Hungary, Algeria, Chile, etc. The typical tripolite forms yellowish-white bands 0·5–1·5 m. thick in beds of clay, gypsum, and "Saugschiefer" (absorbent shale) in a Tertiary basin near Bilin in Bohemia.

In the preparation of the material for the market, that of the purer white quality, after being dug out from open pits, is simply air-dried in the open or in sheds. Organic matter is removed by calcination. Less pure material, containing sand, etc., is treated by washing and sedimentation. Iron is removed by the action of acids.

The varied uses of diatomite depend on its peculiar properties of porosity, lightness, non-conductivity, resistance to heat and acids. It was used by the Greeks and Romans for making light fire-proof tiles ; and in the middle ages was mixed with meal for bread, under the impression that it had a medicinal value. As an absorbent it has been much used with nitroglycerine for the manufacture of dynamite. The so-called dry sulphuric acid is prepared by saturating calcined diatomite with three or four times its weight of acid. Such material can be transported with little risk. Diatomite packed around carboys of acid will soak up leakage in case the vessels become cracked. It has also been used as an absorbent of bromine, disinfectants and liquid manures. On account of its non-conductive properties it is used, sometimes with asbestos, as a light packing material for boilers, steam-pipes, cooking stoves, safes, refrigerators and refrigerating apparatus, fire-proof and sound-proof floors and partitions of buildings, bulkheads of ships etc. Mixed with clay, lime, sawdust, etc., it can be used in the manufacture of fire-proof bricks and tiles; and having a low coefficient of expansion such material is specially adapted for making tubes, models, etc. It is used in the manufacture of various cements and artificial stones. Mixed with magnesia cement it gives a fire-proof cement for stoves ; with shellac, sealing-wax and gramophone records are made. It is also used as a filtering material for liquids and gases ; and various liquids (wine, beer, acids, oil, syrups) can be clarified by stirring with 1% of diatomite and allowing to settle. As a filler it is employed in the manufacture of rubber, cotton fabrics, paints, safety matches, paper, papier-mâché, soap, scouring-powders, tooth-powders, etc. Fused with calcium and magnesium borates it yields a non-cracking glass for glazes and enamels, which can also be used for painting on glass. As a source of silica, it is used in the preparation of sodium silicate, ultramarine, smalt, etc. Finally, as an abrasive (*q.v.*) it, particularly the tripolite variety, is used for polishing metals and stoves. (*Ref.* B. Dammer and O. Tietze, " Die Nutzbaren Mineralien," Stuttgart, 1913, 1 ; "Diatomaceous Earth," Imp. Inst. London, 1928.)

L. J. S.

DIAZINES *v.* Azines.

DIAZO- COMPOUNDS. These organic substances, like the azo- compounds, contain the characteristic group —N_2—, but whereas in the latter series this bivalent radical is invariably attached to two carbon atoms, $C{\cdot}N_2{\cdot}C$, in the former it is generally, although not invariably, combined with only one carbon atom, the other valency being satisfied by : (1) an electro-negative ion $\bar{A}c$ in the *diazonium salts* $C{\cdot}N_2{\cdot}\bar{A}c$; (2) an oxygen atom in the *diazohydroxides* (" *diazo-hydrates* ") $C{\cdot}N_2{\cdot}OH$ and *diazo-oxides* (" *diazotates* ") $C{\cdot}N_2{\cdot}OR$; (3) a nitrogen atom in *diazoamines* (*diazoamino- compounds*)

$$C{\cdot}N_2{\cdot}NHR$$

and *diazoimines* (*azimino-compounds*), which when derived from *ortho*-diamines have a cyclic configuration $C{\cdot}N_2{\cdot}NH{\cdot}C$, whereas those from *para*-diamines are sometimes given a quinonoid structure $N_2{:}CC{:}NH$; (4) a sulphur atom in *diazosulphonates* $C{\cdot}N_2{\cdot}SO_3K$, and *diazosulphides* $C{\cdot}N_2{\cdot}S{\cdot}N_2{\cdot}C$.

The *diazocyanides* $C{\cdot}N_2{\cdot}CN$ contain the azo-group attached to two carbon atoms, one of which belongs to a cyanogen group, and these compounds which, in general, are distinctly coloured, form an intermediate group between the foregoing diazo- derivatives and the azo-compounds.

Certain aliphatic diazo- compounds (*v. infra*) contain the group —N_2— attached by two principal valencies to the same carbon atom.

I. Diazonium Salts.

These diazo- derivatives are generally, but not exclusively, prepared from aromatic amines, and the process, which is termed *diazotisation*, is carried out with the undissociated salt of the amine, and not with the free base. In a hydrolysing solvent like water, it is therefore customary to diazotise aniline and its derivatives with sodium nitrite (1 mol.) and excess (2½ to 3 equivalents) of mineral acid.

The scientific and technical utility of the diazo reaction depends on the ease and rapidity with which three hydrogen atoms of the salt of an aromatic primary amine are replaced by nitrogen from nitrous acid to form the corresponding diazonium salt :

$$ArNH_3Cl+HO{\cdot}NO=ArN_2Cl+2H_2O$$

Aromatic Diazonium Salts.

The diazotisation of the benzenoid and naphthalenoid amines is frequently carried out on a manufacturing scale owing to the employment of aromatic diazonium salts in the production of azo- colouring matters. During the first decade of the present century more than 1,000 tons of para-nitraniline were diazotised annually in the production of " para-nitraniline red." Since 1920 this diazonium salt has been partly replaced by other diazo- derivatives which give azo-pigments faster to light, chlorine, and kier boiling.

The aromatic base is dissolved in dilute hydrochloric or sulphuric acid (3 equivalents in 10–20% aqueous solution) and the solution treated with an equivalent quantity (1 mol.) of sodium nitrite in 10–20% solution. The diazotisation is completed when the liquid contains a slight excess of nitrous acid as indicated by starch and iodide paper.

With aniline and its homologues, the temperature of the diazo- solution is generally maintained at 0–5° to prevent, so far as possible, the decomposition of the unstable diazonium salt, but in other cases, *e.g.* the nitranilines, naphthylamines, benzidine and other diphenyl bases, the diazotisation is carried out most readily at 10°. The aminoanthraquinones are diazotised at 30–40° (Schaarschmidt, Ber. 1916, **49**, 2678).

In alcoholic or acetic acid solution, diazotisation can be effected on the salt of the amine without using an excess of acid, and ethyl or amyl nitrite may, with advantage, be substituted for sodium nitrite. Gaseous methyl nitrite which has been employed in certain diazotisations (J.C.S. 1913, **103**, 1398), is very readily prepared and is a cleaner reagent than amyl nitrite.

When treated with sodium nitrite, aniline hydrochloride in presence of excess of cold hydrochloric acid yields benzenediazonium chloride, whereas in absence of this excess of acid it furnishes diazoaminobenzene.

A product antecedent to either of these diazo- derivatives has been detected by Earl and Hall (J. Proc. Roy. Soc., New South Wales, 1933, **66**, 455), who added 1 mol. of aniline hydrochloride in 40% aqueous solution at −8° to about 1·5 mols. of sodium nitrite in 50% aqueous solution covered with ether and cooled to −15°. A white precipitate separated and dissolved forthwith in the organic solvent. This ethereal solution was dried over anhydrous sodium sulphate and the ether removed under reduced pressure, when a mass of white needles separated consisting of *aniline nitrite*,

$$C_6H_5{\cdot}NH_2,HNO_2$$

(yield about 60%). This salt becomes yellow at room temperature, and its aqueous solution rapidly deposits diazoaminobenzene.

Benzenediazonium chloride, $C_6H_5{\cdot}N_2Cl$, the simplest example of an aromatic diazonium salt, is prepared by adding the calculated quantity of amyl nitrite to aniline hydrochloride suspended in glacial acetic acid at 10°; it is precipitated from the clear solution thus obtained by the addition of ether.

Benzenediazonium sulphate,

$$C_6H_5{\cdot}N_2{\cdot}HSO_4,$$

is prepared in a similar manner from aniline sulphate suspended in glacial acetic acid, the precipitation being effected with alcohol and ether.

Benzenediazonium nitrate,

$$C_6H_5{\cdot}N_2{\cdot}NO_3,$$

which was first precipitated from aqueous solution by ether and alcohol (Griess, Annalen, 1866. **137**, 39), can also be produced in alcoholic or glacial acetic acid solution (Knoevenagel, Ber. 1890, **23**, 2995; Bamberger, *ibid.* 1896, **29**, 446; Hirsch, *ibid.* 1897, **30**, 92; Hantzsch and Jochem, *ibid.* 1901, **34**, 3337).

Diazonium salts have been obtained with a large variety of anions: *platinichlorides, aurichlorides, stannichlorides, ferricyanides, nitroprussiates* (Ber. 1879, **12**, 2119; 1885, **18**, 965), *chromates* (Jahresberichte, 1867, 915; J.C.S. 1905, **87**, 1), *carbonates* and *nitrites* (*ibid.* 1905, **87**, 921), *fluorides* (Ber. 1903, **36**, 2059), *perchlorates* (*ibid.* 1906, **39**, 2713, 3146), *picrates* (J.C.S. 1907, **91**, 1316), *azides* (*ibid.* 1910, **97**, 1697; Ber. 1903, **36**, 2056), *thiosulphates*, *tungstates* (J. Soc. Dyers and Col. 1901, **17**, 279), *thioacetates* (Monatsh. 1907, **28**, 247), *borofluorides* (G.P. 281055) (*v.* Vol. II, p. 43), *phosphomolybdates* and *tungstates* (J.C.S. 1909, **95**, 1319), *arylsulphinates* (Ber. 1911, **44**, 1415), *zincichlorides*, Rev. Gén. Mat. Col. 1914, **18**, 4).

The zincichlorides are frequently used for stabilising diazo- compounds. Dianisidine hydrochloride is bisdiazotised in acid solution to which zinc chloride is added, when the crystalline double zinc salt $(MeO{\cdot}C_6H_3{\cdot}N_2Cl)_2ZnCl_2$ separates. A stabilised diazo- mixture is produced by mixing this zincichloride with partially dehydrated aluminium sulphate or sodium naphthalene tetrasulphonate and drying at 40° to 50° (B.P. 238676). 4-Aminodiphenylamine and its derivatives give stable diazonium zincichlorides and the technical product *variamine blue salt* is of this type.

Diazonium chlorides added to a hydrochloric acid solution of lead tetrachloride furnish a yellow crystalline precipitate diazonium *plumbichloride*,

$$(ArN_2)_2[PbCl_6],$$

which on heating with alcohol gives the chloro-derivative $ArCl$ (Chattaway, Garton and Parkes, J.C.S. 1924, **125**, 1981).

All diazonium salts are endothermic compounds and are liable to explode in the dry state (Berthelot and Vieille, Compt. rend. 1881, **92**, 1076; Sventoslavsky, Ber. 1910, **43**, 1497) and in some cases the explosion point has been determined (Ber. 1899, **32**, 1691; 1900, **33**, 527). The diazonium chromates and perchlorates decompose with considerable violence, and the former have been suggested as explosives (Bull. Soc. chim. 1867, ii, **7**, 270; F.P. 73286).

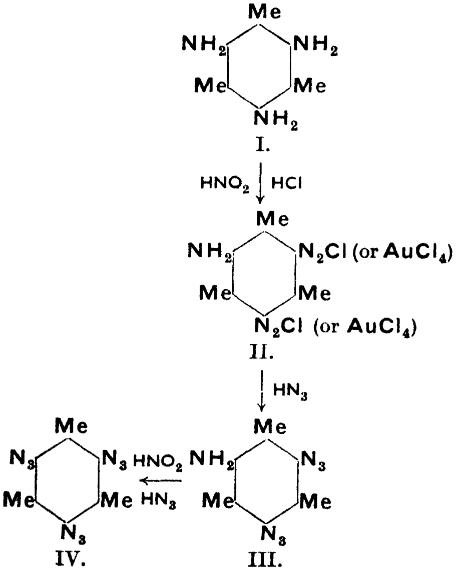
Bisdiazonium salts (*Tetrazo- salts*). These compounds are produced from aromatic diamines.

When the two amino- groups are in the same aromatic nucleus, complete diazotisation is effected only with some difficulty. Metaphenylenediamine hydrochloride and sodium nitrite furnish the azo- colouring matters included under the term "Bismarck brown" (Ber. 1897, **30**, 2111, 2899; 1900, **33**, 2116), but when a solution of the base in excess of hydrochloric acid is added quickly to a large excess of well-cooled aqueous nitrous acid, complete diazotisation takes place and *benzene*-m-*bisdiazonium chloride*, $C_6H_4[N_2{\cdot}Cl]_2$, is produced. When the nitrite is added quickly to the diamine hydrochloride, nitroso-*m*-phenylenediamine results. Para-phenylenediamine hydrochloride, when diazotised in the usual way, gives a mixture of diazonium and bisdiazonium chlorides, but when the hydrochloride is added to excess of nitrous acid, *benzene*-p-*bisdiazonium chloride* is obtained.

Schoutissen (J. Amer. Chem. Soc. 1935, **55**, 4535) has obtained evidence of the diazotisability of *o*-phenylenediamine by treating the diamine in sulphuric acid with nitrosylsulphuric acid and phosphoric acid, for he obtained a small yield of *o*-diiodobenzene on adding potassium iodide. Hodgson and Walker have bisdiazotised all three phenylenediamines by adding the glacial acetic acid solutions to nitrosyl sulphuric acid. On applying the Sandmeyer reaction they obtained from *o*-phenylenediamine a 70% yield of *o*-dichlorobenzene (J.C.S. 1935, 530).

In the naphthalene series, 1:4-naphthylenediamine is diazotised with difficulty, owing to its oxidisability, but in producing its azo- derivatives this difficulty is surmounted by working with its monoacyl- derivatives and diazotising in two stages with an intervening hydrolysis (B.P. 18783, 1891). The heteronucleal naphthylenediamines, excepting the 1:8- compound, can be completely diazotised, yielding *naphthalenebisdiazonium salts* (Ewer and Pick, G.P. 45549, 45788; Badische Anilin und Soda Fabrik, G.P. 130475; Morgan and Micklethwait, J.C.S. 1910, **97**, 2558). Benzidine, tolidine, dianisidine, and other similar heteronuclear diamines of the diphenyl and ditolyl series are readily diazotised, furnishing bisdiazonium salts (*e.g.* *diphenylbisdiazonium chloride*, $Cl{\cdot}N_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl$), which are employed in the manufacture of substantive azo- dyes.

The upper limit of diazotisability in the benzene series has been determined by a study of triaminomesitylene (I), which when treated with nitrosyl sulphate in strong sulphuric acid gives indazole derivatives. However, diazotisation of this triamine was successfully effected in aqueous hydrochloric acid, when even with a large excess of acid and nitrite only two of the three amino groups became diazotised concurrently, and this twofold diazotisation was demonstrated by isolation of aminomesitylenebisdiazonium aurichloride (II) and aminomesitylene bisazoimide (bis-triazomesidine III). The latter compound was produced by adding sodium azide to the diazo- solution.



The non-diazotisability of the third amino-group is not due to steric hindrance, for when the bisdiazonium radicals have been replaced by two triazo groups the resulting bistriazomesidine can still be diazotised, and on further treatment with sodium azide its diazonium salt gives tristriazomesitylene (IV), a compound having the remarkable molecular formula $H_9C_9N_9$, which suggests a polymeride of prussic acid, although this coincidence is merely numerical and not chemical (Morgan and Davies, J.C.S. 1923, **123**, 228).

In an analytical study of the titration of aromatic amines by the diazo- reaction it was found that 1:3:5-triaminobenzene in hydrochloric acid solution gave figures corresponding with threefold diazotisation; 2:4:6-triaminochlorobenzene was completely diazotised only in alcoholic solution (Phillips and Lowy, Ind. Eng. Chem. [Anal.], 1937, **29**, 381).

Velocity of Diazotisation.—Under the usual experimental conditions, diazotisation proceeds with great rapidity, but in $N/1000$ solutions, the velocity of this reaction has been determined by a colorimetric method for estimating the free nitrous acid. The reaction is of the second order, and the values of the constant $C=\frac{x}{t(a-x)}$ are 0·036 for aniline, 0·038 for *p*-toluidine, and 0·041 for *m*-xylidine, with one molecular proportion of free acid at 0°. At higher temperatures the rate is increased (Hantzsch and Schümann, Ber. 1899, **32**, 1691; 1900, **33**, 527; Tassilly, Compt. rend. 1913, **157**, 1148; 1914, **158**, 335, 489). Both colorimetric and electrolytic determinations of the velocity of diazotisation show that, in the absence of disturbing influences, all the aromatic amines are diazotised at the same rate.

Alternative Methods of Producing Aromatic Diazonium Salts.—*Nitrosyl chloride* or *bromide* has been suggested as a diazotising agent (Tilden and Millar, Chem. Soc. Proc. 1894, 59; Kastle and Keiser, Amer. Chem. J. 1895, **17**, 91). *Nitrosyl sulphate* has been used with advantage (Pabst and Girard, D.R.P. 6034; Ber. 1879, **12**, 365; Morgan and Micklethwait, J.C.S. 1910, **97**, 2558). This reagent or sodium nitrite dissolved in concentrated sulphuric acid is employed in diazotising slightly basic amines (Morgan and Evens, J.C.S. 1919, **116**, 1130; *cf.* J. pr. Chem. 1906, [ii], **74**, 275). *Barium nitrite*, when employed in conjunction with sulphuric acid, furnishes diazo- solutions free from inorganic salts (Witt, Ber. 1903, **36**, 4388). The last-named investigator has brought forward an interesting process which consists in dissolving the base in cold concentrated *nitric acid* and adding the calculated amount of *potassium metabisulphite* required to produce sufficient nitrous acid for the diazotisation (Ber. 1909, **42**, 2953).

For unsubstituted aromatic amines the direct method of diazotisation by adding nitrite to the cold acid solutions is generally efficacious, but for amines containing nitro-, carboxyl-, or sulphonic groups the inverted method of mixing the amine with nitrite and running this mixture in cold acid is preferable. Highly substituted amines, such as 4-chloro-2:6-dinitraniline and picramide (2:4:6-trinitroaniline) are dissolved in glacial acetic acid and treated with nitrosylsulphuric acid (Misslin, Helv. Chim. Acta, 1920, **3**, 626; Blangey, *ibid.* 1925, **8**, 780). Schoutissen dissolved highly substituted bases in sulphuric acid and added a solution of nitrosyl sulphuric acid in the same acid. Diazotisation was promoted by diluting the solution with phosphoric acid (sp.gr. 1·70) at 0° (J. Amer. Chem. Soc. 1933, **55**, 4531; Rec. trav. chim. 1935, **54**, 97). Similar methods are used to diazotise amines of the anthraquinone series (J. pr. Chem. 1906, [ii], **74**, 275; Ber. 1904, **37**, 4185).

In the diazotisation of 2:4-dinitro-α-naphthylamine the process is usually attended by the elimination of the *ortho*-nitro- group, and a similar change occurs in the case of certain dinitroanilines. In order to avoid this formation of diazo- oxides it is suggested to diazotise such feeble bases in cold acetic acid with a solution of sodium nitrite in concentrated sulphuric acid. Even 2:4:6-trinitroaniline (picramide) can be diazotised by this process.

This mode of diazotisation may also be employed in converting 2:4:6-trinitro-*m*-phenylenediamine into its bisdiazonium salt (Misslin, Helv. Chim. Acta, 1920, **3**, 626; Meyer and Tochtermann, Ber. 1921, **54**, [B], 2283).

Diazonium bromides are formed by the interaction of *hydrazines* and *diazonium perbromides*

$$2R{\cdot}N_2Br_3+RN_2H_3=3R{\cdot}N_2{\cdot}Br+3HBr$$

(Chattaway, J.C.S. 1908, **93**, 958). An *electrolytic* process for the production of diazonium salts has been patented (Boehringer & Sons, D.R.P. 152926, and B.P. 2608 of 1904).

Diazonium salts can also be prepared from compounds not containing amino- groups; mercury diphenyl and nitrous fumes give benzenediazonium nitrate (Ber. 1897, **30**, 509), and the same salt is produced from nitrosobenzene and nitric oxide in chloroform solution (*ibid.* 1898, **31**, 1528).

Aniline nitrate is transformed into benzene diazonium chloride by zinc and hydrochloric acid (Möhlau, Ber. 1883, **16**, 3080) or by titanous chloride (Knecht, J.C.S. 1924, **125**, 1537).

Certain complex or highly substituted amines resist diazotisation unless treated under pressure (D.R.P. 143450) or with excess of nitrous and mineral acids (Annalen, 1873, **165**, 187; 1891, **260**, 224; Ber. 1900, **33**, 520).

(For indirect methods of forming diazonium salts, *v.* Annalen, 1879, **199**, 320; 1888, **243**, 282; 1892, **270**, 116; Ber. 1893, **26**, 2190; 1899, **32**, 1809; 1900, **33**, 1718; J. pr. Chem. 1896, [ii], **54**, 496; Gazzetta, 1900, **30**, 1526; Bull. Soc. chim. 1891, [iii], **6**, 94.)

Fuming nitric acid reverses the coupling process and regenerates the diazonium salt from its azo- derivatives (Meldola, J.C.S. 1889, **55**, 608; 1894, **65**, 841; O. Schmidt, Ber. 1905, **38**, 3201). Diazonium chlorides are regenerated from azo-dyes by decomposing the latter with chlorine or hypochlorous acid (J. pr. Chem. 1912, [ii], **85**, 325.

REACTIONS OF AROMATIC DIAZONIUM SALTS.

In addition to their power of coupling with phenols, aromatic amines and their sulphonic acids to form the technically important azo- colouring matters, the diazonium salts are synthetical agents of the greatest value, and the following is a synopsis of the principal reactions in which they take part:

1. Decomposition of Diazonium Salts by Water.

(*v.* Ber. 1874, **7**, 1061; 1894, **17**, 2704; 1899, **32**, 1773; 1890, **23**, 3635; 1902, **35**, 89; J. pr. Chem. 1881, [ii], **24**, 476; J.C.S. 1902, **81**, 77; 1903, **83**, 688; 1905, **87**, 5; 1906, **89**, 19).

The decomposition of soluble diazonium salts by water is a unimolecular reaction, and is represented by the well-known equation:

$$k=\frac{1}{t}\log_e\frac{a}{a-x}$$

The relative stability of the diazonium salts is ascertained by comparing the values of the constant k for a given temperature. The most successful method of making this determination consists in heating solutions of the diazo- compounds at a fixed temperature, and measuring the rate at which nitrogen is evolved.

These quantitative decompositions show that the diazonium salts from aniline and *ortho*- and *meta*-toluidine are among the least stable of the series, whereas considerably greater stability is exhibited by the diazotised nitranilines and the diazonium sulphonates derived from the benzenoid and naphthalenoid aminesulphonic acids.

The rate of decomposition of diazo- compounds increases with the temperature and in accordance with Arrhenius's formula for the temperature coefficient (*v.* CHEMICAL AFFINITY, Vol. II, p. 532)

$$\log_e\frac{k_1}{k_2}=\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

The rate of decomposition is independent of the quantity of mineral acid present, and equivalent solutions of benzenediazonium chloride, bromide, sulphate, nitrate, and oxalate decompose with the same velocity; this change is, however, accelerated by colloidal platinum or silver, owing to catalytic action (Hantzsch, Ber. 1900, **33**, 2517; Hausser and Muller, Bull. Soc. chim. 1892, [iii], **7**, 721; 1893, **9**, 353; Compt. rend. 1892, **114**, 549, 669, 760, 1438; Schwalbe, Z. Farb. Ind. 1905, **4**, 433; Ber. 1905, **38**, 2196, 3071; 1909, **42**, 196; Cain, J.C.S. 1902, **81**, 1412; 1903, **83**, 206, 470; 1905, **38**, 2511; Euler, Annalen, 1902, **325**, 292; Veley and Cain, Trans. Faraday Soc. 1909, **5**, 1).

In general, the decomposition of a diazonium salt by water leads to the formation of a phenol:

$$R{\cdot}N_2{\cdot}HSO_4+H_2O=R{\cdot}OH+H_2SO_4+N_2$$

The sulphate is the best salt to employ in this reaction, because the chloride and nitrate are apt to lead respectively to alternative or secondary changes. Benzenediazonium sulphate and its homologues furnish phenol and the cresols and xylenols; diphenyl-4:4′-bisdiazonium sulphate gives rise to 4:4′-dihydroxydiphenyl. Aurin is similarly obtained from diazotised rosaniline (Annalen, 1878, **194**, 306).

In certain cases, more especially in the naphthalene series, the product is contaminated by azo- compounds, resulting from the coupling of the hydroxy- derivative with a portion of the still undecomposed diazonium salt (J.C.S.

1903, **83**, 221). To obviate this difficulty, so far as possible, excess of acid is used in the decomposition. The manufacture of the α-naphtholsulphonic acids (*e.g.* $OH : SO_3H = 1 : 4$ and 1 : 8) from the corresponding α-naphthylaminesulphonic acids furnishes typical examples of the technical application of the process. When the phenolic product is volatile in steam, the normal change is facilitated by operating with solutions boiling above 100°. A good yield of guaiacol is obtained by adding the diazo- salt of *ortho*-anisidine to a mixture of sodium sulphate and dilute sulphuric acid boiling at 135–145°, the volatile product being removed at the moment of formation (Kalle & Co., B.P. 7233 of 1897 ; *cf.* Annalen, 1889, **253**, 281 ; Ber. 1874, **7**, 1008 ; D.R.P. 167211 ; J.C.S. 1906, **89**, 19 ; *cf.* Willstätter and Schudel, Ber. 1918, **51**, 782).

Secondary reactions occur even in the simplest cases where the boiling is protracted (Ber. 1890, **23**, 3705), and in many instances, owing to the great stability of the diazo- compound, not a trace of the hydroxy- derivative can be isolated (Amer. Chem. J. 1889, **11**, 319; Cain, J.C.S. 1003, **83**, 688).

(For other exceptional decompositions of diazo- compounds by water, *v.* Ber. 1874, **7**, 1061 ; 1884, **17**, 2704; 1899, **32**, 1773; 1902, **35**, 89; J.C.S. 1896, **69**, 1327 ; 1902, **81**, 77 ; 1905, **87**, 5 ; 1906, **89**, 19).

The diazo- compounds are very sensitive to light, which induces the phenolic decomposition even in certain cases where the action of hot water or acids is very slight (J.C.S. 1907, **91**, 35 ; *cf.* Compt. rend. 1881, **92**, 1074 ; Ber. 1890, **23**, 3131 ; 1901, **34**, 1668 ; D.R.P. 53455, 56606 ; J.S.C.I. 1890, **9**, 1001).

2. Decomposition of Diazonium Salts by Alcohols.

The reaction between diazonium salts and alcohols may proceed in two different ways :

1. $R{\cdot}N_2X + C_2H_5{\cdot}OH = R{\cdot}H + CH_3{\cdot}CHO + N_2 + HX$

2. $R{\cdot}N_2X + C_2H_5OH = R{\cdot}O{\cdot}C_2H_5 + N_2 + HX$

The former of these changes was originally regarded as the general reaction, but more recent researches have shown that the second is the normal change. The factors determining the course of the reaction are, however, numerous and complicated, involving (1) the nature of the alcohol ; (2) the influence of substituents in the diazonium salt ; (3) the pressure and temperature at which the decomposition is affected.

The tendency to replace the diazo- group by hydrogen increases with the molecular weight of the alcohol employed. Benzenediazonium chloride or sulphate and methyl alcohol give anisole exclusively. With ethyl alcohol, these salts yield chiefly phenetole, but benzene is also produced. The diazonium sulphates from *p*-chloro- and *p*-bromo-aniline furnish only *p*-chloro- and *p*-bromo-benzene with ethyl alcohol, but with methyl alcohol they give rise mainly to the methyl ethers of *p*-chloro- and *p*-bromo-phenol (Amer. Chem. J. 1898, **20**, 229 ; *cf.* Annalen, 1871, **159**, 191; Ber. 1901, **34**, 3337 ; 1903, **36**, 2061 ; Amer. Chem. J. 1893, **15**, 518 ; 1897, **19**, 531, 547, 561).

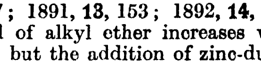
The diazo- salts of the simpler amines (aniline and its homologues) react chiefly in the direction indicated by the second of the foregoing equations, and yield mixed ethers, but the presence of acid substituents

$$(Cl, Br, NO_2, CO_2H, NH{\cdot}SO_2R)$$

favours the predominance of the first change. The nitranilines (*ortho*-, *meta*-, and *para*-) give respectively 87, 51, and 40% of nitrobenzene, the 1:2-, 2:1-, and 1:4-nitronaphthylamines furnish the corresponding nitronaphthalenes, whereas α- and β-naphthylamines yield α- and β-ethoxynaphthalenes (Remsen and others, Ber. 1885, **18**, 65 ; Amer. Chem. J. 1886, **8**, 243 ; 1887, **9**, 587 ; 1891, **13**, 153 ; 1892, **14**, 15).

The yield of alkyl ether increases with rise of pressure, but the addition of zinc-dust or an alkali (sodium hydroxide or ethoxide, potassium carbonate) inhibits almost entirely the formation of mixed ether and leads to the substitution of the diazo- group by hydrogen (Amer. Chem. J. 1893, **15**, 105, 301, 320, 379 ; 1894, **16**, 235 ; 1895, **17**, 454 ; 1897, **19**, 163, 531 ; 1898, **20**, 298 ; 1904, **31**, 119).

The simultaneous elimination of two diazonium groups by the reducing action of ethyl alcohol has been applied successfully to a series of heterocyclic diamines, the diamino-*cyclic* 1:3-diazalines, of which the following base (formula I) is the simplest example. This diamine and its analogues are diazotised by Schoutissen's method with nitrosyl-sulphuric acid in concentrated phosphoric acid and after dilution the soluble bisdiazonium salt is reduced in solution by boiling alcohol. The resulting *cyclic* 1:3-diazaline (formula II) is extracted with ether (Morgan and Stewart, J.C.S. 1938, 1292).



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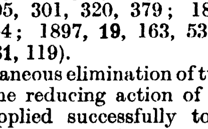


II.

3. Replacement of the Diazo- Group by Hydrogen.

In addition to the action of alcohol, the diazo- group can be eliminated by the use of a variety of reducing agents :

(i) The diazonium salt is reduced to the corresponding ***hydrazine*** and the hydrazino- group $NH{\cdot}NH_2$ removed by boiling with ***copper sulphate*** (Baeyer and Pfitzinger, Ber. 1885, **18**, 90, 786).

(ii) Reduction of the diazo- compound with ***alkaline sodium stannite*** (Friedländer, Ber. 1889, **22**, 587).

(iii) By various other reducing agents, ***stannous formate*** (Ber. 1885, **18**, 357 ; J. pr. Chem. 1889, [ii], **40**, 97), ***hypophosphorous acid*** (Ber. 1902, **35**, 162), ***sodium hyposulphite*** (*ibid.*

1907, **40**, 858), *formic acid* and *copper powder* (*ibid.* 1890, **23**, 1632), *aluminium powder* in alcohol (Morgan and Evens, *l.c.*).

4. Replacement of the Diazo- Group by Halogen, Cyanide, Cyanate, and Thiocyanate Radicals.

Fluorine may be introduced into the aromatic nucleus in place of the diazo- group by treating the diazonium salt with hydrofluoric acid. Diazoamino- compounds (*v. infra*) are also employed in bringing about this replacement, and when treated with concentrated hydrofluoric acid they yield the corresponding fluoro-derivative; fluorobenzene is thus produced from diazoaminobenzene or diazobenzene-piperidide (J. pr. Chem. 1870, [ii], **1**, 395; Ber. 1875, **8**, 893; 1879, **12**, 581; 1889, **22**, 1846).

A general and more convenient method of introducing fluorine into the aromatic nucleus consists in adding 40% borofluoric acid to the diazo- solution from the aromatic base when the corresponding aryldiazonium borofluoride is precipitated. These borofluorides are generally very stable salts ; they are not explosive and may be crystallised from warm water. When a diazonium borofluoride is gently heated it evolves nitrogen and boron trifluoride, whilst fluorine replaces nitrogen in the aromatic ring. Thus benzenediazonium borofluoride (decomposing at 121–122°) furnishes fluorobenzene, b.p. 85°/760 mm. Toluene-*p*-diazonium borofluoride (decomp. 110°), *m*-xylene-4-diazonium borofluoride (decomp. 108°), and naphthalene-*a*-diazonium borofluoride (decomp. 113°) give respectively *p*-fluorotoluene, 4-fluoro-*m*-xylene, b.p. 143–144°, and *a*-fluoronaphthalene, b.p. 110°/17 mm.

The bisdiazonium salts from benzidine yield the corresponding bisdiazonium borofluoride (95% yield, decomp. 137–138°), and this salt is pyrolysed into 4:4′-difluorodiphenyl (b.p. 115–116°/11 mm., 80% yield).

m- and *p*-Phenylenediamines are similarly converted into bisdiazonium borofluorides which yield respectively *m*-difluorobenzene, b.p. 82–83°/752 mm., m.p. −59°, and *p*-difluorobenzene, b.p. 88·5°/767 mm., m.p. −13° (Balz and Schiemann, Ber. 1927, **60**, [B], 1186; Schiemann and Bolstad, *ibid.* 1928, **61**, [B], 1403; *cf. ibid.* 1929, **62**, [B], 1794, 1805; 1930, **63**, [B], 3035). *p*-Nitrobenzenediazonium borofluoride decomposes smoothly into *p*-fluoronitrobenzene.

The first really successful process for replacing the diazo- group by *chlorine* (or *bromine*) was discovered by Sandmeyer ; it consists in adding the diazotised solution to cuprous chloride (or bromide) dissolved in warm hydrochloric (or hydrobromic) acid, when nitrogen is evolved and the corresponding chloro- or bromo-derivative is produced (Ber. 1884, **17**, 1633, 2650; 1885, **18**, 1492, 1496; 1886, **19**, 810; 1890, **23**, 1628, 1880; Annalen, 1893, **273**, 141).

The first stage in the *Sandmeyer reaction* is considered to be the formation of an additive compound of diazonium salt and cuprous chloride ; the decomposition of this intermediate product proceeds readily only above a certain temperature, which is different for each diazonium salt (Erdmann, Annalen, 1893, **272**, 141; *cf.* Votoček, Chem. Zeit. Rep. 1896, **20**, 70; Hantzsch and Blagden, Ber. 1900, **33**, 2544). The substitution of bromine for diazo-nitrogen follows a similar course (Phil. Trans, 1864, **154**, 673; Annalen, 1866, **137**, 49; Amer. Chem. J. 1891, **13**, 486; Gazzetta, 1890, **20**, 631).

The foregoing substitutions are also effected by the addition to solutions of diazonium chlorides or bromides of finely divided copper or the copper bronze of commerce (Gattermann, Ber. 1890, **23**, 1218; 1892, **25**, 1074; Ullmann, *ibid.* 1896, **29**, 1878; *cf.* Angeli, *ibid.* 1891, **24**, 952).

Iodine is readily substituted for the diazo-complex by treating the acid diazo- solutions with potassium iodide even in the absence of copper or cuprous salts.

As an alternative to the Sandmeyer and Gattermann reactions, the replacement of a diazonium group by chlorine or bromine is effected by converting the diazonium salt either into mercurichloride by adding mercuric chloride in aqueous potassium chloride or into mercuribromide by adding mercuric bromide or nitrate in aqueous potassium bromide. The double diazonium mercurihalide is dried by washing with acetone, methyl alcohol or ether, mixed with twice its weight of potassium chloride or bromide and heated until the diazo- compound is completely decomposed. This procedure is effective in the following cases: 2:2′-diaminodiphenyl (2:2′-xenylenediamine) is converted into 2:2′-dichlorodiphenyl or 2:2′-dibromodiphenyl (yield 80%); *p*-bromobenzenediazonium bromide with mercuric bromide and potassium bromide gives *p*-dibromobenzene, and *β*-naphthylamine is converted similarly into 2-bromonaphthalene (yield 65%). The double diazonium salts with antimony trichloride and stannic chloride may be utilised in a similar manner (Schwechten, Ber. 1932, **65**, [B], 1605).

Benzenediazonium chloride when treated with potassium and mercuric iodides in methyl alcoholic solutions yields successively

$$C_6H_5{\cdot}N_2{\cdot}HgI_3 \text{ and } (C_6H_5N_2)_2HgI_4.$$

Both are yellow compounds decomposing at 63–64° and 65° respectively. When maintained at the ordinary temperature these mercuric iodides pass mainly into iodobenzene and mercuric iodide with loss of nitrogen, but in addition the former gives a 10% and the latter a 3% yield of diphenyliodonium tri-iodomercuriate $[(C_6H_5)_2I]HgI_3$, yellow crystals, m.p. 171·8° (Nesmejanov, Z. anorg. Chem. 1929, **178**, 300).

The Sandmeyer reaction includes the important synthetical operation of replacing the diazo- group by a *cyanide* radical, the diazonium salt being added to a warm solution of potassium cuprocyanide. The Gattermann process is also applicable to this synthesis, the addition of copper powder to a mixture of diazonium salt and potassium cyanide inducing a similar replacement. The *cyanate* radical is introduced in the place of the diazo- group by adding successively to a solution of diazonium salt, potassium cyanate and copper powder (Gattermann, Ber. 1890, **23**, 1218; 1892, **25**, 1086). The *thiocyanate* group is introduced by adding potassium thiocyanate and cuprous thiocyanate to a solution of diazonium sulphate (Gattermann and Hausskneeht, Ber. 1890, **23**, 738 ; Thurnauer, *ibid.* 770).

Although cuprous halides are employed in the Sandmeyer reaction for replacement of diazo- group by chlorine or bromine, nickel cyanide is better than cuprous cyanide for the introduction of cyanogen, and ferric salts are the best catalysts for introduction of the thiocyanogen (**CNS**) group (Compt. rend. 1926, **183**, 421).

5. Replacement of the Diazo- Group by Sulphur and Sulphur-containing Radicals.

These reactions are of importance as furnishing methods for the synthetical production of sulphonic acids.

Thiophenols or *disulphides* are obtained by treating diazonium salts with potassium xanthate and then hydrolysing the resulting aromatic xanthate (Leuckart, J. pr. Chem. 1890, [ii], **41**, 179 ; *cf.* Klason, Ber. 1887, **20**, 349 ; Walter, Chem. Soc. Proc. 1895, **11**, 141). Phenyl sulphide is produced by treating benzenediazonium salts with hydrogen sulphide or ammonium sulphide (Graebe and Mann, Ber. 1882, **15**, 1683). Benzenoid diazonium salts yield sulphides on treatment with sodium cuprous thiosulphate, but diazotised α-naphthylamine only gives α-azonaphthalene (Börnstein, Ber. 1901, **34**, 3968).

The replacement of a diazonium by a *sulphinic* group is effected by saturating with sulphur dioxide an acid solution of diazonium sulphate and adding copper powder; nitrogen is evolved and the resulting sulphinic acid extracted with ether (Gattermann, Ber. 1899, **32**, 1136; B.P. 26139 of 1896; D.R.P. 95830).

The foregoing thiophenols, disulphides and sulphinic acids yield the corresponding *sulphonic acids* on oxidation (D.R.P. 70286 ; B.P. 11865 of 1892).

6. Replacement of the Diazo- Group by Nitro-, Nitroso-, and Amino- Radicals.

The introduction of a *nitro-* group is brought about either by heating the diazonium salt with nitrous acid and cuprous oxide or by mixing the diazonium sulphate with cupro-cupric sulphite and adding excess of alkali nitrite. By the latter process, 2:4:6-tribromobenzenediazonium sulphate gives 65% of 1-nitro-2:4:6-tribromobenzene and diazotised β-naphthylamine gives 25% of β-nitronaphthalene, a substance prepared with considerable difficulty by other processes (Sandmeyer, Ber. 1887, **20**, 1497 ; Hantzsch and Blagden, 1900, **33**, 2544). The diazonium borofluorides have been utilised in effecting a replacement of the diazo- group by a nitro-radical. A thin aqueous paste of the borofluoride was added to a suspension of copper in aqueous sodium nitrite. The following reaction takes place at room temperature :

$$\mathrm{Ar{\cdot}N_2{\cdot}BF_4 + NaNO_2 = Ar{\cdot}NO_2 + N_2 + NaBF_4}$$

In this way a 64% yield of *p*-dinitrobenzene was obtained from *p*-nitraniline, and ethyl *p*-aminobenzoate furnished a 50% yield of *p*-nitrobenzoic acid (Starkey, J. Amer. Chem. Soc. 1937, **59**, 1479). The introduction of a *nitroso-* group is effected by treating a diazonium chloride with alkaline potassium ferricyanide (Bamberger and Storch, Ber. 1893, **26**, 471). The addition of hydroxylamine to a solution of diazonium salt results in the regeneration of the original amine (Mai, Ber. 1892, **25**, 372 ; 1902, **35**, 2593, 3920).

7. Formation of Azoimides.

The introduction of the azimino- group $\mathrm{N_3}$ into the aromatic nucleus is effected by the following reactions: (1) action of hydroxylamine on diazonium sulphates (Mai, Ber. 1892, **25**, 372 ; 1893, **26**, 1271 ; Forster and Fierz, J.C.S. 1907, **91**, 855, 1350); (2) interaction of ammonia and diazonium perbromides ; (3) direct action of sodium azide on diazonium salts in excess of sulphuric acid (Nölting and Michael, Ber. 1893, **26**, 86 ; Forster and Fierz, J.C.S. 1907, **91**, 1942). The last of these processes is carried out so readily that the production of an aziminocompound may be used to estimate the number of diazo- groups in a diazonium salt (Meldola and Hawkins, Chem. Soc. Proc. 1892, **8**, 133; Morgan and Micklethwait, J.C.S. 1910, **97**, 2560). Aromatic azoimides are also produced by the interaction of chloroamine, $\mathrm{NH_2Cl}$, and diazonium chlorides (Forster, J.C.S. 1915, **107**, 260), and by removing water from the nitrosoarylhydroxylamines.

These aryl azoimides can be employed synthetically as a means of transforming an amine into the corresponding aminophenol as when warmed with moderately concentrated sulphuric acid, two-thirds of the nitrogen is eliminated and a hydroxyl group is introduced into the nucleus (Friedlander and Zeitlin, Ber. 1894, **27**, 192 ; Morgan and Porter, J.C.S. 1915, **107**, 651).

The interaction of sodium azide and diazocompound leads directly to the formation of a triazo- derivative in practically quantitative yield. A noteworthy alternative arises when a diazonium salt interacts with an arylsulphonamide in alkaline solution. The reactions are fairly general and the yields favourable.

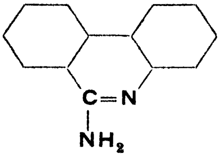
$$\mathrm{R{\cdot}SO_2{\cdot}NH_2 + R'{\cdot}N_2Cl}$$
$$\mathrm{= R{\cdot}SO_2H + R'N_3 + HCl}$$
$$\mathrm{R{\cdot}SO_2{\cdot}NH_2 + 2R'{\cdot}N_2Cl}$$
$$\mathrm{= R{\cdot}SO_2{\cdot}N_2{\cdot}R' + R'N_3 + 2HCl}$$

The former reaction affords a means of producing arylsulphinic acids (Dutt, Whitehead and Wormall, J.C.S. 1921, **119**, 2088).

Miscellaneous substitutions, v. J.C.S. 1888, **53**, 460; Amer. Chem. J. 1888, **10**, 368; Ber. 1902, **35**, 1964.

For the replacement of the diazo- group by arsinic and stibinic complexes consult ARSENICALS, ORGANIC, and ANTIMONIALS, ORGANIC.

The primary amines of the triazole and thiazole series yield diazonium salts with oxyacids (nitrates or sulphates) which are more stable than the corresponding chlorides. Primary amines of the pyridine and quinoline series having the amino- group *ortho-* or *para-* with respect to tertiary nitrogen atom yield very unstable diazonium chlorides which decompose forthwith into chloro-pyridines or quinolines. 9-Aminophenanthridine (I) does not diazotise normally in acid solution, but reacts slowly with nitrous acid, giving phenanthridone II (Morgan and Walls, J.C.S. 1932, 2227). The other amino- derivatives of phenanthridine are readily diazotisable.



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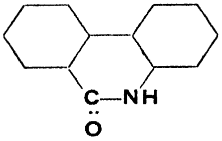


II.

Condensations effected by Means of Aromatic Diazonium Salts.

Azo- compounds are formed, to a slight extent, during the Sandmeyer reaction, and this condensation takes place to a greater extent when the usual order of mixing is reversed and the cuprous chloride added to the cold solution of diazonium salt. Aniline, *o*-chloraniline, and *o*- and *p*-toluidine give considerable quantities of azo- derivatives, but the nitranilines and their homologues furnish diphenyl compounds (Niementowski, Ber. 1901, **34**, 3325; Ullmann and Forgan, *ibid.* 3802; D.R.P. 126961). Cuprous oxide dissolved in ammonia or hydroxylamine also promotes the diphenyl condensation (Annalen, 1902, **320**, 122), diphenyl itself being readily prepared by adding copper, zinc or iron powder to benzenediazonium sulphate in dilute alcohol (Ber. 1890, **23**, 1226); ββ-dinaphthyl is similarly produced from β-diazonaphthalene sulphate (J.C.S. 1895, **67**, 653). 2:2′-Dimethyl-1:1′-dianthraquinonyl results from the condensation of 2 mols. of 2-methylanthraquinone-1-diazonium sulphate when stirred with acetic anhydride and copper bronze powder (Scholl and Kunz, Ber. 1907, **40**, 1697; B.P. 14578 of 1905).

Coupling of Diazonium Salts.

2:4:6-Trinitrobenzenediazonium salt is highly reactive and couples with mesitylene to form the azo- compound $C_6H_2(NO_2)_3{\cdot}N_2{\cdot}C_6H_2Me_3$. This reaction recalls a similar interaction between negatively substituted diazonium salts and certain unsaturated hydrocarbons containing conjugated ethylene linkings. Thus the azo-compound $CH_2{:}CMe{\cdot}CMe{:}CH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$ is readily obtained from dimethylbutadiene and *p*-nitrobenzenediazonium chloride in glacial acetic acid. This condensation product is reduced by tin and hydrochloric acid to the aminohydrazine,

$$CH_2{:}CMe{\cdot}CMe{:}CH{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2.$$

Other diolefins such as butadiene (erythrene), isoprene, and α-methylbutadiene (piperylene) also couple with the active diazo- derivatives from *p*-nitroaniline and 2:4-dinitroaniline (Meyer and Schoeller, Ber. 1919, **52**, [B], 1468).

Diazonium compounds in general couple with ethers of a carboxylated naphthol, thus 2-methoxy-3-naphthoic acid couples in aqueous solution with the diazo- derivative of *p*-chloroaniline, 2:4-dichloroaniline, *p*-nitroaniline, 4-nitro-*o*-anisidine, benzidine, tolidine, *o*-, and *m*-nitroanilines, sulphanilic acid, and 5-nitro-*o*-anisidine. The first six diazo- derivatives give unmethylated dyes, the next three give a mixture of approximately equal parts of unmethylated and methylated dyes, the last diazo- compound couples without demethylation (Jambuserwala and Mason, J. Soc. Dyers and Col. 1930, **46**, 339).

Reactive diazonium salts couple in the side chains of unsaturated aromatic compounds. *p*-Nitrobenzenediazonium sulphate in alcoholic solution reacts with anethole,

$$CH_3{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

to give anisaldehyde-*p*-nitrophenylhydrazone. With *iso*safrole, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{:}CH_3$, this diazo- compound gives piperonal-*p*-nitrophenylhydrazone, and with *iso*apiole,

$$CH_2O_2{:}C_6H(OMe)_2{\cdot}CH{:}CH{\cdot}CH_3,$$

apiolaldehyde-*p*-nitrophenylhydrazone is obtained. A similar condensation occurs with *iso*eugenol, which yields vanillin-*p*-nitrophenylhydrazone. These condensations distinguish aromatic compounds containing the propenyl group $—CH{:}CH{\cdot}CH_3$ from those (*e.g.* safrole) with the allyl side chain $—CH_2{\cdot}CH{:}CH_2$. In the former cases the reactive diazo- derivative, probably in its tautomeric form,

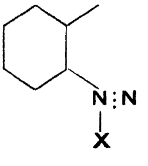
$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NO,$$

attacks at the unsaturated linking, forming a hydrazone of the aromatic aldehyde with rupture of the side chain and elimination of acetaldehyde (Quilico and others, Gazzetta, 1928, **58**, 389; 1929, **59**, 39).

The rate of coupling of diazonium salts with phenols in buffer solutions of constant ionic strength ($\mu=0{\cdot}24$) has been measured colorimetrically. Over a wide range of concentration the rate of reaction corresponds with that calculated by means of the bimolecular equation. Rate of coupling is a simple function of the p_H of the solution: $\log k=\log k_0+p_H$ (Conant and Petersen, J. Amer. Chem. Soc. 1930, **52**, 1220).

Benzenediazonium salts couple with 2:6-diaminopyridine first to a diazoamino- compound, the hydrochloride of which on boiling in aqueous solution gives 2:6-diamino-3(or 4)-benzeneazopyridine (U.S.P. 1820483). 6-Chloro-3-aminopyridine (or the corresponding 6-iodo-base) is diazotised and coupled with a variety of reactive pyridine bases such as 2:6-diaminopyridine and its 3-bromo- and 3-iodo- derivatives, to give heterocyclic azo- derivatives which are useful bactericides (B.P. 341598).

The product obtained by tetrazotising *o*-phenylenediamine in nitrosylsulphuric-phosphoric acid solution couples in this strongly acid medium with phenol, β-naphthol, anisole, phenetole and even mesitylene to yield *o*-diazo-azo-compounds so that in such circumstances the bisdiazotised compound should be represented by the formula



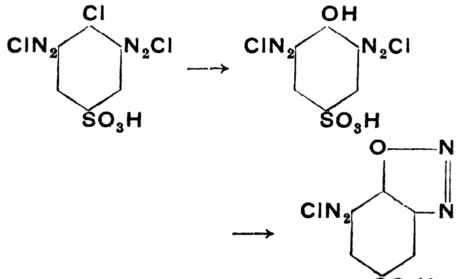
in order to explain the one-sided coupling. When the acidity of the solution is reduced then a second coupling with a phenolic compound takes place giving rise to *o*-diazo dyestuffs of outstanding stability towards alkali (Schoutissen, Rec. Trav. Chim. 1938, **57**, 713).

INTERCHANGE OF GROUPS IN DIAZONIUM SALTS.

The diazonium salts of the more highly substituted amines frequently undergo remarkable transformations, some of which have been suggested for use in the technical production of azo- compounds.

The dinitroanisidines, containing nitro- groups either in *ortho*- or *para*- positions with regard to the amino- group, exchange these radicals for hydroxyl during the process of diazotisation. In certain instances, the methoxyl group present in these compounds undergoes demethylation, etc., with the production of internal diazo-oxides (quinonediazides). The nitro- group is set free in the form of nitrous acid, which continues the diazotisation process on further quantities of the base (Meldola and others, J.C.S. 1900, **77**, 1172; 1901, **79**, 1076; 1902, **81**, 988; 1905, **87**, 1205). Methoxyl or chlorine radicals in *para*- positions with respect to the diazo- complex are rendered labile by contiguous nitro- groups so that *para*-diazo- oxides are produced (Klemenc, Ber. 1914, **47**, 1407; Morgan and Porter, J.C.S. 1915, **107**, 653), but an accumulation of acidic (nitro-) groups favours the removal of adjacent nitro- groups and the formation of *ortho*-diazo- oxides (Meldola and Reverdin, J.C.S. 1910, **97**, 1204). A sulphonic group is replaced by hydroxyl in the diazotisation of *m*-phenylenediaminedisulphonic acid (B.P. 18283 of 1903), and certain of the dinitronaphthylamines, when diazotised, yield internal diazo-oxides, owing to the initial replacement of a nitro- group by hydroxyl (Gaess and Ammelburg, Ber. 1894, **27**, 2211; Friedländer, 1895, **28**, 1951; *cf.* Meldola and Streatfeild, J.C.S. 1895, **67**, 908).

The replacement of an acidic (electronegative) substituent by hydroxyl frequently occurs on treating the diazonium salt with alkalis.



A sulphonic acid group may be similarly eliminated as in *β*-naphthylamine-1:5:7-trisulphonic acid which, when diazotised and treated with weak alkali, yields naphthylene-2-diazo-1-oxide-5:7-disulphonic acid (G.P. 141750; B.P. 16811, 20551 of 1901; 1561, 6615, 23993 of 1902; 16995, 27372, of 1903; 4997 of 1904).

These replacements sometimes take place even when the diazo- solutions are diluted with water, or spontaneously when the diazonium base is present as the salt of a weak acid (acetate, oxalate, carbonate, etc.) (*v.* Orton, Proc. Roy. Soc. 1902, **71**, 153; J.C.S. 1903, **83**, 796; 1907, **91**, 1554; Noelting and Battegay, Ber. 1906, **39**, 79).

p-Chlorobenzenediazonium thiocyanate

$$Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}CNS$$

undergoes a remarkable molecular transformation when dissolved in alcohol containing a trace of hydrochloric acid. The thiocyanate and chlorine radicals change places, and on adding ether to the solution, *p*-thiocyanobenzene diazonium chloride is precipitated (Hantzsch, Ber. 1896, **29**, 947). Similarly, 2:4:6-tribromobenzenediazonium sulphate in presence of excess of potassium thiocyanate is converted into 2:4:6-trithiocyanobenzenediazonium thiocyanate and many brominated diazonium chlorides pass into chlorinated diazonium bromides (Ber. 1897, **30**, 2334; 1898, **31**, 1253; 1900, **33**, 505; *cf.* J.C.S. 1902, **81**, 1376). The last of these transformations has been studied quantitatively, and the following generalisations have been established:

(i) Bromine atoms are replaced by chlorine only when present in the *ortho*- or *para*- position with respect to the diazonium group, those in *ortho*- positions being most readily removed. A bromine atom in the *meta*- position is not affected.

(ii) The ease of transformation increases with the number of bromine atoms present.

(iii) The transformation constant, calculated from the equation for a unimolecular reaction $k=1/t(\log A/A-x)$, increases with the temperature and is also influenced by the solvent, having its minimum value in water, and becoming greater as the series of alcohols is ascended.

(iv) Diazonium salts containing two bromine atoms are stable when dry, but are rapidly transformed in ethyl alcohol; 2:4:6-tribromobenzenediazonium chloride becomes transformed in the dry state.

These changes do not occur either with iodinated diazonium chlorides or with brominated diazonium fluorides (Hantzsch, Ber. 1903, **36**, 2069).

STABILISED DIAZO- COMPOUNDS.—The technical utility of stable diazo- compounds has led to many devices for preventing the decomposition of the diazonium group which otherwise occurs on keeping the salts even at the ordinary temperature. When mixed with an equal weight of crystalline alum or aluminium sulphate about two-thirds dehydrated, diazo- compounds may be stored for long periods without deterioration. The diazo- derivative of the technically important 5-nitro-*o*-toluidine is stabilised by precipitation as borofluoride (B.P. 316691).

Diazonium borofluorides are rendered more stable by adding to the solid salt or to its solution an acid or an acid salt such as hydrochloric acid, borofluoric acid, potassium tetroxalate, sodium hydrogen sulphate, or dibutylnaphthalene-β-sulphonic acid (B.P. 317355). Stable diazonium metallofluorides are obtained by interaction of diazo- solutions with titanofluoric acid or the corresponding complex fluoro acids containing aluminium, stannic, antimonious, antimonic, or zinc fluorides. The products are isolated from concentrated solutions by strong cooling (B.P. 332227). The solubility of certain diazonium borofluorides is increased by addition of salts of metals of periodic groups I and III, such as alkali chlorides (including ammonium chloride), alum, or aluminium chloride, B.P. 332630. *p*-Chlorobenzenesulphonic acid (or its salts) furnishes a stabilising anion when added to diazo- solutions derived from nitranilines, chloronitranilines, chloro- or nitrotoluidines, or any non-sulphonated derivative of these or similar bases. The products are crystalline, water-soluble, stable diazonium *p*-chlorobenzenesulphonates which may be dried at moderate temperatures (B.P. 265985, 273352). Aromatic diazo- compounds react with aldehyde-bisulphite derivatives of ammonia or amines to furnish soluble stable diazoamino- compounds of the general type

$$Ar{\cdot}N{:}N{\cdot}NR{\cdot}CHR'{\cdot}O{\cdot}SO_2Na.$$

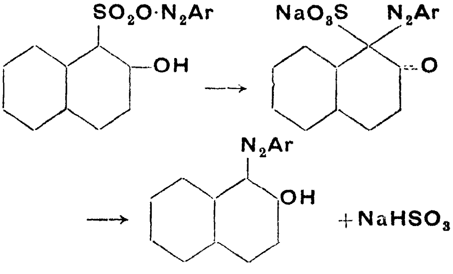
These diazoamines regenerate diazo- salts by the action of mineral acids. Diazotised 5-nitro-*o*-toluidine couples with the formaldehyde-bisulphite compound of ammonia, methylamine, or dimethylamine. Such diazoamines are used in dyeing and in the protection of plants from insect pests (B.P. 309610).

A preparation which will liberate a diazo-compound when dissolved in cold water is obtained on adding solid sodium nitrite to a mixture containing 1 mol. of an aromatic nitrobase (such as *p*-nitraniline) rather more than 1 mol. of sulphuric acid (or the equivalent proportions of the sulphate of the base and bisulphates) and a suitable diluent such as partly dehydrated aluminium sulphate or alum, arylsulphonates or mixtures of arylsulphonates and partly dehydrated alum. Such preparations are very stable, and diazotisation is effected on addition of water (G.P. 426033).

Moderately soluble diazonium fluorosulphonates are obtained by interaction of diazo-compounds and fluorosulphonic acid. These products are insensitive to shock and decompose on heating without explosion; they are used in dyeing and against insect pests (B.P. 303527).

In the manufacture of soluble azo-dyes, diazonium salts are generally employed in aqueous solution, but solid diazo- compounds, in dry or paste form, have been introduced to enable dyers to prepare "ingrain" azo- colours which are developed on the textile fibres.

Aryl sulphonic acids have been employed in this stabilisation of diazo- process, including α- and β-naphthalenesulphonic acids and naphthalene-1:5-disulphonic acid (Marriott, J. Soc. Dyers and Col. 1936, 52, 172). Anisole-*p*-sulphonic acid and acylaminobenzenesulphonic acid also give rise to stable diazonium salts. The diazonium salts of β-naphthol-α-sulphonic acid behave in the peculiar manner indicated in the following diagram:



The first change is effected under the influence of alkali when the hemiquinonoid salt dissolves and the solution when acidified yields a precipitate of the insoluble azo-β-naphthol, the sulphonic group having been eliminated as bisulphite. If the Ar radical contains a nitro-group, as in the nitranilines, and if excess of alkali is used a deep-seated change occurs and a dihydrophthalazine is formed (Rowe and others, J.C.S. 1931, 1965; 1933, 1067; 1935, 1796).

Dried mixtures of an aromatic primary amine, sodium nitrite and an acid salt give rise to diazo-compounds on dissolving in water. A mixture of nitrite, β-naphthol, and arylamine-formaldehydebisulphite $Ar{\cdot}NH{\cdot}CH_2{\cdot}SO_3Na$, give a clear solution in weak alkali, but when printed may be developed by acid treatment, which hydrolyses away the ω-sulphonate group, the primary base, $Ar{\cdot}NH_2$, thus liberated is diazotised in acid solution and couples with the naphthol. I.C.I. (B.P. 374497).

LIGHT-SENSITIVE DIAZO- COMPOUNDS.—The sensitivity to light of many diazo- compounds has led to various suggestions regarding the application of these compounds to photography.

Diazosulphonates, made from diazonium salts and sodium sulphite, are incapable of coupling in alkaline solutions with phenols or aromatic diamines, but exposure to light removes this inhibition so that a coloured image is produced wherever light has acted. Feer, in 1889, suggested for this purpose an alkaline mixture of ditolylbisdiazosulphonate (derived from tolidine) and resorcinol, α-naphthol, or *m*-phenylenediamine. In 1890, Green, Cross and Bevan patented the primuline process based on the decomposition by light of the diazo- compound of primulin or other thioamines. Paper or linen impregnated with diazoprimuline or diazodehydrothio-*p*-toluidine was exposed to light, and subsequently immersed in a bath of a phenol or other coupling base. Resorcinol gives an orange tint, β-naphthol a red, 2:4-tolylenediamine a reddish-brown, and α-naphthylamine a violet tint. Of other light-sensitive diazo- compounds may be mentioned *o*-diazosalicylic acid, 1-diazo-2-oxynaphthalene-4-sulphonic acid. *Ozalide papers*, which have largely displaced blueprint paper, are based on the principle that a light-sensitive diazoanhydride may be mixed with a phenol or aromatic amine without coupling until the mixture is rendered slightly alkaline. On exposure to light the sensitive diazoanhydride is decomposed except where it is protected. The paper base is then rendered alkaline by gaseous ammonia when coupling occurs between the undecomposed diazoanhydride and the phenol or aromatic amine with formation of a coloured azo- compound.

Stabilised diazonium salts, such as metallic double salts and borofluorides (*see* preceding section) from diazotised *p*-aminoalkylanilines and *p*-aminodiphenylamine and its derivatives are employed in preparing *diazotype paper*. On exposure to light under a stencil the diazonium salt is destroyed in parts and the unchanged salt is coupled with phloroglucinol to obtain deep shades approaching black or with resorcinol to give brown tints (B.P. 281604, 234818, 443995; Chem. Age, 1936, **34**, 198).

Other diazotype papers contain both diazo-compound and coupling component. The diazo-derivative is selected as one giving a diazo- oxide which in acid media is incapable of coupling with a phenol. 1-Diazo-2-naphthol-4-sulphonic acid is an example of this group; it remains uncoupled with a phenol, especially if boric acid or a titanium salt is present. Exposed under a tracing the diazo- group is destroyed, and on bringing the paper into a warm ammoniacal atmosphere coupling occurs without addition of further reagents (B.P. 210826; G.P. 419978). Prints are also obtainable with a diazo- component alone, providing that this substance can couple with its decomposition product. The foregoing 1-diazo-2-naphthol sulphonic acid will do this, as will also diazotised *o*-aminosalicylic acid (G.P. 111416). Diazo- compounds have also been utilised in colour photography (Murray, Phot. J. 1933, April, and B.P. 363616).

CONSTITUTION OF AROMATIC DIAZONIUM SALTS.

Aromatic diazonium salts are generally soluble in water to a neutral solution, thus showing, by an absence of hydrolytic dissociation, that the diazonium base is a stronger base than the aromatic amine from which it was derived. The strength of the diazonium base has been confirmed by physico-chemical measurements.

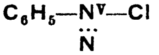
Determinations of the electrical conductivity of solutions of benzenediazonium chloride and nitrate show that the benzenediazonium radical is strictly comparable with other quaternary ammonium ions. The rate of migration of the benzenediazonium ion at 25° is 45·7, the corresponding constants for the methylpyridinium and tetramethylammonium ions being 44·3 and 43·6 respectively. The molecular electrical conductivity of solutions of diazonium salts increases with dilution, just as in the case of the corresponding potassium and ammonium compounds.

The affinity constant of benzenediazonium hydroxide at 0° is 70 times greater than that of ammonium hydroxide, and somewhat exceeds that of piperidine. The affinity constants of *p*-methoxybenzenediazonium and *ψ*-cumidinediazonium hydroxides are even greater, and approximate closely to those of the alkali hydroxides. A comparison of the electrical conductivity experiments, with the results obtained in the hydrolysis of ethyl acetate by benzenediazonium hydroxide, shows that in *N*/128 solutions at 0°, approximately 33% of the base exists in the ionised condition (Ber. 1890, **23**, 3220; 1895, **28**, 1737; 1898, **31**, 1612).

Benzenediazonium (*Diazobenzene*) behaves like an alkali or a complex ammonium cation.

Benzenediazonium hydroxide (*Diazobenzene hydrate* or *hydroxide*) is only known in solution, and is produced by treating aqueous benzenediazonium chloride with the calculated amount of silver oxide, or by adding barium hydroxide to a solution of benzenediazonium sulphate (Hantzsch, Ber. 1898, **31**, 340). The solution is strongly alkaline, and gives at once an azo- compound with *β*-naphthol; the dissolved base decomposes, however, fairly rapidly even at 0°.

The striking similarity in the physical and chemical properties of the diazonium and quaternary ammonium salts suggests the existence of quinquevalent nitrogen in the former compounds, and on these grounds the following formula, formerly proposed by Blomstrand (1869), Strecker (1871), and Erlenmeyer (1874), has now been generally adopted for benzenediazonium chloride and its homologues:



$$\begin{array}{l} C_6H_5-N^{V}-Cl \\ \qquad\quad\ \vdots \\ \qquad\quad\ N \end{array}$$

although, for many years, the alternative configuration, $C_6H_5 \cdot N = N \cdot Cl$, suggested by Kekulé, was usually employed.

The close analogy existing between the diazonium and alkali salts is shown further by the facility with which both series yield double salts with cobaltic nitrite and with the chlorides of platinum, gold and mercury. Diazonium perhalides are also known, corresponding with the perhalides of potassium, rubidium, cæsium and quaternary ammonium bases (Hantzsch, Ber. 1895, **28**, 1736, 2754).

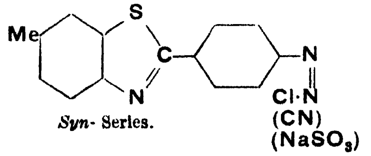
The benzenoid diazonium salts with colourless anions (nitrates, sulphates, chlorides) are generally colourless, but the corresponding bromides, iodides and thiocyanates are coloured, and the deeper the colour the more explosive the salt. When cooled in liquid air, these coloured salts become less coloured; moreover, their aqueous solutions are colourless.

The development of colour and increase in explosibility are considered by Hantzsch to indicate a change in constitution, the coloured substance being regarded as an equilibrium mixture of diazonium salt and *syn*-diazo-compound (*v. infra*). This equilibrium is disturbed in the sense of forming more of the colourless diazonium salt by lowering the temperature or by dissolving the substance in water (Hantzsch, Ber. 1897, **33**, 2179; **1900**, **33**, 2179; Euler, Ber. 1895, **31**, 4168). But although in the benzene series the diazonium chlorides, nitrates and sulphates are colourless, yet in the diphenyl and naphthalene series many diazonium salts with these anions are coloured and comparatively stable. Moreover, this colour (yellow or orange) is retained either in aqueous solution or at the temperature of liquid air. Apart from their colour, these salts have all the properties of the simpler diazonium salts (neutral solutions, coupling with phenols, etc.). These facts indicate that increase in the complexity of the organic portion of the diazonium cation leads to the development of colour in normal diazonium salts.

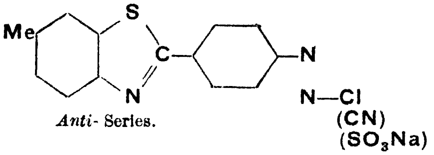
STEREOCHEMISTRY OF DIAZO- DERIVATIVES.—The stereochemistry of diazo- compounds advocated by Hantzsch, and accepted generally by workers in this field of organic chemistry, is based on the existence of two isomeric forms of aromatic diazocyanides, diazosulphonates and diazo-oxides. Of these two series the more stable *anti*-diazo- compounds have frequently been prepared in a state of purity so that their existence has been confirmed by many analyses. The labile *syn*-diazo- compounds, on the other hand, are much less readily isolated, and analytical data in support of their existence as definite chemical entities are not always obtainable. 4′-Amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine) was shown by its discoverer A. G. Green (1889) to give rise to a diazo-chloride quite stable in solution at the ordinary temperature.

When suspended in absolute alcohol and diazotised with ethyl nitrite, the hydrochloride of the foregoing aminothiazole yields two isomeric compounds, an insoluble diazochloride and a soluble one precipitated by ether. *Syn*-1-phenyl-5-methylbenzothiazole-4′-diazochloride decomposes at 139°, dissolves readily in water, couples immediately with alkaline α-naphthol, and evolves nitrogen with copper bronze, giving 4′-chloro-1-phenyl-5-methylbenzothiazole. *Anti*-1-phenyl-5-methylbenzothiazole-4′-diazochloride decomposes at 270°, is insoluble in water, does not couple with alkaline β-naphthol until after treatment with hydrochloric acid. With copper bronze and this acid it remained unchanged for several hours, but after a week yielded the chloro-derivative.

Ice-cold solutions of the *syn*-diazochloride when treated with sodium sulphite gave a sodium *syn*-1-phenyl-5-methylbenzothiazole-4′-diazosulphonate, a salt which couples with β-naphthol. At the ordinary temperatures (about 20°) a non-coupling *anti*-diazosulphonate is obtained. Similar experimental conditions lead to the formation of *syn*- and *anti*-1-phenyl-5-methylbenzothiazole-4′-diazocyanides. The *syn*-diazocyanide is a brick-red product, very soluble in water and decomposes at 131°, it couples readily with alkaline β-naphthol and readily loses nitrogen with copper bronze. The *anti*-diazocyanide, a deep orange precipitate insoluble in water, melts at 175°, does not couple with alkaline β-naphthol, and evolves nitrogen only very slowly with copper bronze. Accepting the stereochemical hypothesis these three pairs of *syn*- and *anti*-diazo- compounds may be thus represented :



Syn- Series.



Anti- Series.

The solubility in water of the *syn*-diazochloride and -diazocyanide suggests that these compounds pass readily into the diazonium condition, D being the thiazole radical (Morgan and Webster, J.C.S. 1921, **119**, 1071).

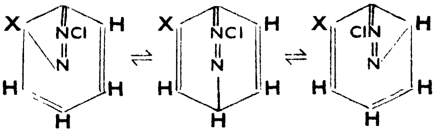
$$\begin{array}{l} \mathrm{D-N} \\ \quad \| \; x\mathrm{H_2O} \\ \mathrm{Cl-N} \end{array} \rightleftharpoons \left[\begin{array}{l} \mathrm{D-N} \\ \quad ||| \; x\mathrm{H_2O} \\ \quad \mathrm{N} \end{array}\right]\mathrm{Cl}$$

In this benzothiazole series there was also qualitative evidence of the existence of *syn*- and *anti*-diazo-oxides (diazotates). For the constitution of diazo-oxides (diazotates), *see* Angeli, Ber. 1926, **59** [B], 1400 ; Hantzsch, *ibid.* 1929, **62**, [B], 1235 ; Quilico, Gazzetta, 1931, **61**, 326.

(*Coloured diazonium salts*, *v.* Hantzsch, Ber. 1900, **33**, 3183 ; 1901, **34**, 4168 ; Annalen, 1900, **312**, 126 ; Cain, J.C.S. 1905, **87**, 5 ; Morgan and others, *ibid.* 1907, **91**, 1311, 1505 ; 1908, **93**, 614 ; 1909, **95**, 1319.)

The idea embodied in Blomstrand's diazonium formula (*v. supra*) fails to express one important point, namely, the dependence of the stability of the diazo- complex on the presence of an unsaturated group. Yet this is a matter of fundamental importance, for hitherto no amine in which the basic nitrogen is attached to a fully saturated ring or complex has yielded a diazonium salt.

Cain has suggested an alternative formula, (2), giving expression to this circumstance (J.C.S. 1907, **91**, 1051), in which the diazonium salt is represented as having a *para*-hemiquinonoid constitution ; and this conception has been extended by Morgan (*ibid.* 1908, **93**, 617 ; 1910, **97**, 2563) so as to include the equally admissible *ortho*-hemiquinonoid configurations (1) and (3) :

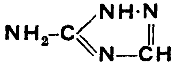


(1) (2) (3)

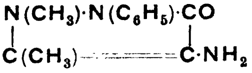
Euler has also advocated a *para*-hemiquinonoid structure for diazonium salts (Ber. 1908, **41**, 3979).

NON-AROMATIC DIAZONIUM SALTS.

The foregoing hypotheses of the constitution of aromatic diazonium salts, which bases their existence on the unsaturated nature of the aromatic complex, accord with the fact that certain non-aromatic primary amines containing unsaturated organic groups manifest, in some degree, the property of diazotisability. Among these bases are aminotriazole (I) and its derivatives, and aminoantipyrine (II) :



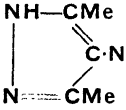
I.



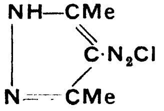
II.

(Thiele and Manchot, Annalen, 1898, **303**, 33 ; Knorr and Stolz, *ibid.* 1896, **293**, 67 ; *cf.* Ber. 1900, **33**, 1158 ; 1906, **39**, 2925 ; Annalen, 1900, **312**, 133). In addition to amino- derivatives of the pyrazoline group (Michaelis, Annalen, 1906, **350**, 288), the 4- and 5-amino derivatives of the pyrazole group give rise to remarkably stable diazonium salts (Morgan and Reilly, J.C.S. 1914, **105**, 436 ; Michaelis and others, Annalen, 1911, **385**, 1 ; 1915, **407**, 229, 274 ; Mohr, J. pr. Chem. 1914, [ii], **90**, 509). 2-Aminothiazole, a heterocyclic base containing sulphur and nitrogen in the ring, furnishes diazonium salts of the oxyacids (Morgan and Morrow, J.C.S. 1915, **107**, 1291).

Pyrazole Series.—Among pyrazole bases the effect of orientation on the stability of the diazonium salts is well marked.

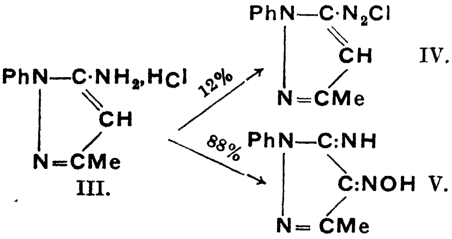


I.

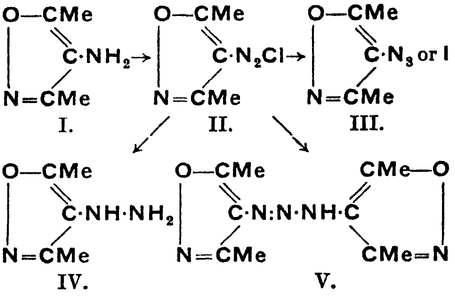


II.

When diazotised in the usual manner, 4-amino-3:5-dimethylpyrazole (I) yields the diazonium chloride (II) stable in either hot aqueous solutions or up to 150° in the dry state. When the diazo- group is in position 5 the product is much less stable, for 1-phenyl-3-methyl-4-ethylpyrazole-5-diazonium chloride decomposes quickly even at room temperature. If the 4-ethyl group is replaced by labile hydrogen as in 1-phenyl-3-methyl-5-aminopyrazole hydrochloride (III), then nitrous acid yields only 12% of diazonium salt (IV), the main product (88%) being the imino-oxime (V) (Mohr, J. pr. Chem. 1914, **90**, (ii), 509).

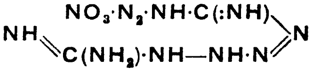


iso-*Oxazole Series.*—3:5-Dimethyl*iso*oxazole has been converted into 4-nitro-3:5-dimethyl*iso*oxazole, and the latter reduced by amalgamated aluminium and moist ether to 4-amino-3:5-dimethyl*iso*oxazole (I), which diazotises to the very soluble diazonium chloride (II). This diazo- derivative is less stable than the foregoing 3:5-dimethylpyrazole-4-diazonium chloride.



3:5-Dimethyl-*iso*-oxazole-4-diazonium chloride interacts readily with sodium azide or potassium iodide to yield respectively 4-triazo-3:5-dimethyl*iso*-oxazole (III) and 4-iodo-3:5-dimethyl*iso*-oxazole (III), pale yellow needles, m.p. 52·5–54°. On reduction this diazonium chloride gives a hydrazine (IV), and it couples with its parent base to furnish a colourless diazoamine (V) (Morgan and Burgess, J.C.S. 1921, **119**, 698, 1546).

Distinct evidence of diazotisability has been adduced in the indole and pyrrole series (Angeli and d'Angelo, Atti R. Accad. Lincei, 1904, [v], **13**, i, 258 ; Angelico, *ibid.* 1905, [v], **14**, ii, 167). It has also been shown (K. A. Hofmann, Hock and Roth, Ber. 1910, **43**, 682, 1087) that aminoguanidine gives rise to diazonium salts, derived, however, not from the salts of aminoguanidine itself, but from a more complex molecule containing two guanidine residues, and having a greater degree of unsaturation. The diazonium nitrate, for example, is represented by the formula :



$$\begin{array}{l} \qquad NO_3\cdot N_2\cdot NH\cdot C(:NH)\diagdown \\ NH \qquad\qquad\qquad\qquad\qquad\quad N \\ \qquad \diagdown C(NH_2)\cdot NH-NH\cdot N \diagup\!\!\diagup \end{array}$$

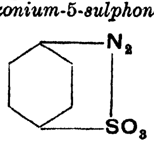
containing a diazo- complex associated with an open chain having three unsaturated linkings.

II. Cyclic Diazo- Compounds.

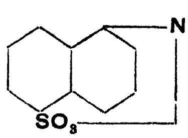
In certain instances, the action of nitrous acid on substituted aromatic amines leads to the formation of compounds having their diazo-nitrogen in a cyclic complex, this result being due to the subsequent interaction of a substituent group.

1. Internal Diazonium Salts.

Sulphonated amines of the benzene and naphthalene series furnish diazo- derivatives which are generally misnamed *diazo-sulphonic acids.* These compounds, however, do not contain ionic hydrogen, and are really internal diazonium salts ; No. 1, the so-called "*diazobenzenesulphonic acid*," being *benzenediazonium-*p*-sulphonate*, whilst No. 2 is *naphthalene-1-diazonium-5-sulphonate.*



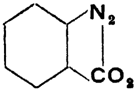
(1)



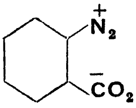
(2)

These internal diazonium sulphonates are of great technical importance in the manufacture of azo- dyes. They are prepared either by adding sodium nitrite to an acid suspension of the amino sulphonic acid or by acidifying a solution containing nitrite and the alkali salt of the aminosulphonic acid (Rev. prod. chim. 1917, **20**, 21).

Of a similar nature are the cyclic diazo-derivatives obtained by diazotising aromatic aminocarboxylic acids (*cf.* Bülow and Haas, Ber. 1911, **44**, 601), *e.g.* " *diazo-anthranilic acid* " or *benzenediazonium*-o-*carboxylate*


(3)

or

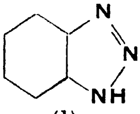

(3*a*)

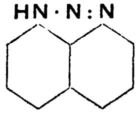
which is employed in the production of methyl red (*v.* Chemical Analysis, Acidimetry and Alkalimetry, Vol. II, p. 641).

These internal diazonium salts are now often formulated as polar substances, Formula (1) being modified as $\overset{+}{N_2}\cdot C_6H_4\cdot \overset{-}{SO_3}$ and the last-mentioned diazonium carboxylate as shown in formula (3 *a*).

2. Cyclic Diazo- Compounds due to Internal Condensation.

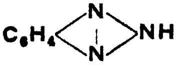
Aromatic *ortho-* and *peri-*diamines do not yield diazonium salts except in special circumstances (Schoutissen, J. Amer. Chem. Soc. 1935, **55**, 4535 ; Hodgson and Walker, J.C.S. 1935, 530), inasmuch as their interaction with nitrous acid leads very readily to the formation of cyclic *diazoimines* (*Azimino- compounds*)

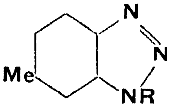

(1)

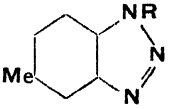

(2)

Phenylene-o-diazoimine (1) (*Aziminobenzene*) and **naphthylene-1:8-diazoimine** (2) (1:8-*Azimino-naphthalene*) are typical members of this series of diazo- compounds.

The triazole rings thus set up are remarkably stable, and in the case of the *ortho-* derivatives (1) are not opened by mineral acids without complete rupture of the molecule. The peri-diazoimines (2) occupy a position intermediate between the ortho-diazoimines (1) and the para-diazoimines (*v. infra*).

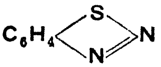
The 1:2- and 2:3-naphthylene-diamines furnish respectively 1:2- and 2:3-*naphthylene-diazoimines* (1:2- and 2:3-*azimino-naphthalenes*). (Constitution of ortho-diazoimines and their acyl- derivatives, Griess, Ber. 1882, **15**, 2195; Kekulé, Lehrbuch, ii, 739 ; Morgan and Godden, J.C.S. 1910, **97**, 2557 ; *cf.* Ber. 1874, **7**, 316; 1876, **9**, 221 ; 1887, **20**, 2999; 1894, **27**, 874; Annalen, 1889, **255**, 344 ; J.C.S. 1906, **89**, 4). Although Griess's formulation for the azimino- compounds  $C_6H_4<\overset{N}{\underset{N}{|}}>NH$ still persists in chemical literature, it has been disproved completely, and that of Kekulé substantiated by the preparation of three pairs of isomerides having respectively the following formulæ, where R=acetyl, benzoyl, or benzenesulphonyl.





This form of isomerism could not exist with Griess's symmetrical configuration (Morgan, Micklethwait and Scharff, J.C.S. 1913, **103**, 1394; 1914, **105**, 117). Although these diazoimines do not couple with phenols and aromatic bases to form azo- dyes, yet employment has been found for them in the production of synthetic carbazole derivatives which are obtained on heating these cyclic diazo- compounds (Ullmann, Ber. 1898, **31**, 1697 ; 1914, **47**, 380).

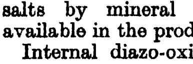
Similar stable cyclic diazo- compounds are obtained by diazotising the *ortho*-aminothiophenols, **o-phenylenediazosulphide** being a colourless crystalline substance with a sweetish odour and feebly basic properties



(Jacobson, Annalen, 1893, **277**, 209, 218, 232, 237).

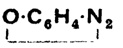
3. Cyclic Diazo- Compounds due to Combined Internal Condensation and Salt Formation.

In this group are found certain diazo-derivatives of amines containing slightly acidic substituents in *ortho-* or *para-* but not *meta-* positions with respect to the aminic nitrogen.

(i) **Internal diazo-oxides** are produced from *ortho-* and *para-* aminophenols and their derivatives. In some cases an intermediate diazonium salt is formed which condenses to the diazo-oxide on treatment with silver oxide or an alkali (Schmitt, Ber. 1868, **1**, 67 ; Hantzsch and Davidson, *ibid.* 1896, **29**, 1522 ; Cameron, Amer. Chem. J. 1898, **20**, 229). The first diazo-compound prepared by Griess (Annalen, 1858, **106**, 123), namely, **dinitrobenzenediazo-oxide**,  $(NO_2)_2C_6H_2<\overset{O}{\underset{N_2}{|}}$, belongs to this class; it is produced by diazotising picramic acid, and has been utilised in the production of azo- colours. The 1:2-, 2:1-, 2:3-, and 1:8-amino-naphthols and their sulphonic acids similarly give rise to internal diazo-oxides which are so stable that they can be nitrated. These internal diazo-oxides are readily transformed into diazonium salts by mineral acids, and are therefore available in the production of azo- dyes.

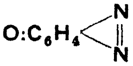
Internal diazo-oxides can also be produced by leaving the diazonium salts of highly substituted amines (*e.g.* 2:4:6-trichloroaniline) in aqueous solutions containing no free mineral acid (Orton, Proc. Roy. Soc. 1903, [illegible] J.C.S. 1903, **83**, 796).

These diazo- derivatives have been formuated either as cyclic diazo-oxides (I) or as quinonediazides (II) :



$O{\cdot}C_6H_4{\cdot}N_2$

I.



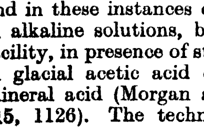
$O{:}C_6H_4{<}N{=}N$

II.

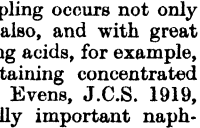
(*cf.* Wolff, Annalen, 1900, **312**, 126 ; Morgan and Micklethwait, J.C.S. 1908, **93**, 607).

Repeated attempts to prepare internal diazo-oxides from *m*-aminophenol and its nitro-derivatives, which have been quite unsuccessful, strengthen the view that these diazo- derivatives are to be regarded as quinonediazo-oxides (II), with the reservation that similar compounds are producible from 1:8-aminonaphthol, 'H acid,' and other *peri-* derivatives (Morgan and Porter, J.C.S. 1915, **107**, 645). In the case of aminophenolsulphonic acids the $NH_2{:}OH=1{:}2$ compounds give these coloured *o*-quinonediazides; the $NH_2{:}OH=1{:}4$ compounds yield diazonium sulphonates changing to *p*-quinonediazides on partial neutralisation ; the $NH_2{:}OH=1{:}3$ compounds give rise only to diazonium sulphonates which lose diazo-nitrogen and furnish complex azo- derivatives on treatment with alkali (Morgan and Tomlins, J.C.S. 1917, **111**, 497).

AROMATIC DIAZO-OXIDES. — 2:4-Dinitro-α-naphthylamine is a feeble base which is diazotised by adding nitrosyl sulphate (chamber crystals) or dry sodium nitrite to the base dissolved in cold concentrated sulphuric acid, the solution being subsequently diluted with fragments of ice. The liquid is then poured into a large excess of ice-water, when a crystalline brownish-yellow precipitate of 4-nitronaphthalene-1-diazo-2-oxide (I) is obtained.



I.



II.

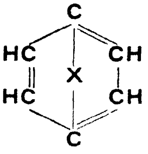
This remarkably stable diazo-oxide couples only with the more reactive phenols such as resorcinol, phloroglucinol and 1:3-dihydroxynaphthalene, and in these instances coupling occurs not only in alkaline solutions, but also, and with great facility, in presence of strong acids, for example, in glacial acetic acid containing concentrated mineral acid (Morgan and Evens, J.C.S. 1919, **115**, 1126). The technically important naphthalenediazo-2-oxide-4-sulphonic acid II forms an acidic brown copper compound which gives no precipitate with sodium hydroxide and a yellow solution with ammonia (Battegay and Schmidt, Bull. Soc. chim. 1927, (iv), **41**, 205).

For the diazotisation of aminophenols which are readily oxidised to quinones, nitrites are employed in presence of mineral acids and salts of copper, iron, zinc or similar metals. The resulting diazo- solutions may be used either for coupling to form azo- dyes or for displacement of the diazo- group by hydrogen, halogens or other substituents (G.P. 431513).

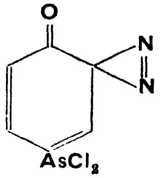
Aminophenylarsine dichlorides and aminophenylstibine dichlorides diazotise to yield compounds of the type $Cl_2X{\cdot}C_6H_4{\cdot}N_2Cl$ (where $X=As$ or Sb). The arsenical derivative on treatment with sodium hydrogen carbonate is converted into a *p*-phenylarsonic acid

$$(I\ ;\ X=AsO{\cdot}OH)$$

which on reduction with sulphur dioxide in presence of iodine yields *p*-phenylenechloroarsine (I ; $X=AsCl$).



I.



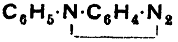
II.

3-Amino-4-hydroxyphenylarsinic acid when similarly treated gives first the diazo- salt $AsCl_2{\cdot}C_6H_3(OH)N_2Cl$, which readily loses hydrogen chloride to pass into the arsenical quinonediazide (II) (Schmidt and Hoffmann, Ber. 1926, **58**, [B], 555, 560).

(ii) *para*Diazoimines and diazoimides.

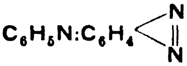
p-Diazoiminobenzene and derivatives.—The earliest known derivative of *p*-diazoiminobenzene was obtained by the action of alkali on diazonium salts of *p*-aminodiphenylamine (Ikuta, Annalen, 1888, **243**, 282 ; Hantzsch, Ber. 1902, **35**, 895).

The following alternative formulæ (III and IV) have been given to this product :



$C_6H_5{\cdot}N{\cdot}C_6H_4{\cdot}N_2$

III.



$C_6H_5N{:}C_6H_4{<}N{=}N$

IV.

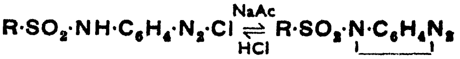
corresponding respectively with the foregoing formulæ (I and II) for the internal diazo-oxides. Successive nitration of the phenyl group gradually increases the stability of these *p*-diazoimines (Morgan and Micklethwait, J.C.S. 1908, **93**, 604).

The arylsulphonyl derivatives,

$$Ar{\cdot}SO_2N{:}C_6H_4{:}N_2,$$

were first discovered by Morgan and Micklethwait in 1905, and the simplest acyl derivative, formyl-*p*-diazoiminobenzene, was isolated by Morgan and Upton in 1917).

The *para*-diazoimides are produced from the acyl- and arylsulphonyl- derivatives of the *para*-diamines, and similar products are obtained from the arylsulphonyl-1:8-naphthylenediamines. The production of these diazoimides takes place in two stages, the diazonium salt first produced being decomposed by sodium acetate or mild alkali, yielding the internal condensation product :



$$\underset{\text{V.}}{R{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl} \overset{NaAc}{\underset{HCl}{\rightleftharpoons}} \underset{\text{VI.}}{R{\cdot}SO_2{\cdot}N{\cdot}C_6H_4N_2}$$

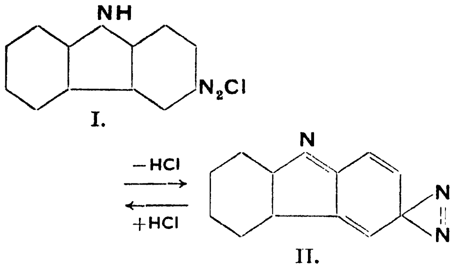
These *para*-diazoimides (VI) are yellow, sparingly soluble substances readily reconverted by strong acids into the corresponding diazonium salts. They combine additively with phenols, naphthols, naphthylamines and their sulphonic acids, yielding azo- colouring matters (Morgan and Micklethwait, J. Soc. Dyers and Col. 1909, **25**, 107 ; *cf.* J.C.S. 1905, **87**, 74, 921, 1302 ; 1906, **89**, 1162 ; 1907, **91**, 1509 ; 1908, **93**, 615; Badische Anilin- und Soda-Fabrik, G.P. 205037).

The foregoing general reaction has been extended further by the device of diazotising with liquid nitrogen trioxide in an anhydrous solvent such as acetone. In this way the simplest members of the series $Ac{\cdot}N{:}C_6H_4{:}N_2$ have been obtained containing formyl, acetyl, and benzoyl groups (Morgan, Upton, and Cleage, J.C.S. 1917, **111**, 187 ; 1918, **113**, 588.

3-Aminocarbazole hydrochloride gives rise to a very stable yellow diazonium chloride

$$C_{12}H_8N_3Cl,3H_2O$$

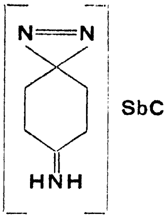
which becomes anhydrous when stored *in vacuo* over sulphuric acid. With sodium azide it yields a colourless 3-triazocarbazole, m.p. 176–177°.



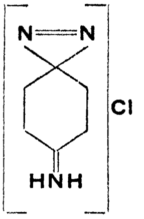
When carbazole-3-diazonium chloride (I) is treated in the cold with ammonia in the absence of light, hydrogen chloride is removed and carbazole-3-diazoimine (II) is precipitated in bright orange-red needles darkening at 80–90° and exploding at 95°. This diazoimine is extremely photo-sensitive and decomposes almost immediately in sunlight. It couples with phenols and reactive aromatic amines, and on addition of hydrochloric acid regenerates the diazonium chloride (I) (Morgan and Read, J.C.S. 1922, **121**, 2711).

In 1926 W. H. Gray obtained the hydrochloride and double antimony chloride of *p*-diazoiminobenzene itself by the following series of reactions.

The hydrochloride of acetyl-*p*-phenylenediamine was diazotised and treated with antimony trichloride when bis-*p*-acetaminobenzenediazonium chloride-antimony chloride separated as a yellow crystalline precipitate, m.p. 147°. When decomposed with water this double salt furnished *p*-acetaminobenzenediazonium chloride, m.p. 131°, which on hydrolysis with boiling dilute hydrochloric acid yielded *p*-diazoiminobenzene-hydrochloride-antimony trichloride (I), decomposing at 179°, and this double salt on treatment with water furnished p-*diazoiminobenzene hydrochloride* (II), a yellow substance exploding at 155°. Both the corresponding picrate and chromate explode at 160°.



I.



II.

In bright sunlight acetic anhydride converts the foregoing hydrochloride into *p*-acetaminobenzenediazonium chloride.

Acetyl-*m*-phenylenediamine hydrochloride when diazotised and combined with antimony trichloride gives bis-*m*-acetaminobenzenediazonium hydrochloride-antimony trichloride, m.p. 94°, which, unlike its *para*-isomeride, is decomposed on warming with dilute acid, but when treated successively with cold water and chromic acid yields an explosive *m*-acetaminobenzenediazonium chromate. There is no indication in this meta-series of the formation of a diazoimine similar to the above compound (II) (J.C.S. 1926, 3174).

III. Diazoamines.

The diazoamines or diazoamino- compounds have the general formula $XN_2{\cdot}NHY$, and may be either aromatic, mixed aromatic-aliphatic, or aliphatic in character, according as to whether X and Y are aromatic or aliphatic hydrocarbon radicals.

1. AROMATIC DIAZOAMINES.

The aromatic diazoamines are produced (1) by the action of nitrous acid (1 mol.) on two molecular proportions of a primary benzenoid amine ; (2) by coupling a diazonium salt with a primary or secondary benzenoid amine.

Diazoaminobenzene, $C_6H_5{\cdot}N_2{\cdot}NH{\cdot}C_6H_5$, yellow crystals, m.p. 98°, is produced in quantitative yield by dissolving 10 parts of aniline in two parts of water containing 12 parts of hydrogen chloride, diazotising with 8 parts of sodium nitrite, and adding the diazo- solution to a solution of 10 parts of aniline in the calculated amount of hydrochloric acid. The diazoamine is precipitated on the addition of sodium acetate. (Absorption spectrum of diazoaminobenzene, Purvis, J.C.S. 1914, **105**, 590.)

When warmed with aniline containing aniline hydrochloride, diazoaminobenzene is transformed into *p*-aminoazobenzene, the velocity of transformation obeying the law of unimolecular reactions. When the transformation occurs below 40° a small proportion (about 4%) of *o*-aminoazobenzene is produced (F. H. Witt, Ber. 1912, **45**, 2380 ; 1913, **46**, 2557).

Diazoaminobenzene is conveniently prepared in a state of purity by passing carbon dioxide into an aqueous alcoholic solution of aniline and sodium nitrite. The product recrystallised from alkaline alcohol separates in lemon yellow needles, m.p. 99·5–100°. Dilute acids cause a lowering of this melting-point. When the action of cold glacial acetic acid on diazoaminobenzene is allowed to proceed until it is nearly all transformed into aminoazobenzene a non-basic product of this reaction is isolated on diluting the liquid with water, when a tarry mass is deposited from which by repeated crystallisation a deep red substance, *benzenediazoaminoazobenzene*, $C_6H_5N_2\cdot C_6H_4\cdot NH\cdot N_2\cdot C_6H_5$, is obtained (m.p. 119·5°), identical with the compound produced by coupling diazotised aminoazobenzene and aniline. It is extremely difficult to separate this substance from diazoaminobenzene, and mixtures of the two substances which melt lower than either compound have in the past suggested the existence of an isomeric and more fusible diazoaminobenzene (Earl, J. Proc. Roy. Soc., New South Wales, 1930, **64**, 97). Interesting observations on the transformation of diazoaminobenzene into aminoazobenzene have also been made by Rosenhauer (Ber. 1928, **61**, [B], 392 ; 1930, **63**, [B], 1056 ; 1931, **64**, [B], 1438), who holds that this transformation is due to primary fission into diazonium salt and aniline followed by nuclear coupling and not to isomeric change. The conversion is effected not only by glacial acetic acid, but also by dilute aqueous acetic acid or formic acid, never by quinoline and its hydrochloride. Benzenediazonium chloride and aniline hydrochloride couple at 0° to give aminoazobenzene hydrochloride without intermediate formation of diazoaminobenzene. About 70% of aminoazobenzene is obtainable in acetic acid solution if 3–4 mols. of aniline are added.

Diazoamino-*p*-toluene,

$$C_7H_7\cdot N_2\cdot NH\cdot C_7H_7,$$

similarly prepared to diazoaminobenzene, undergoes transformation into an *ortho*-azo- compound, but the velocity of this change is only about one-ninth of that of the preceding transformation to *para*-azo- derivative.

The coupling of diazonium salts with metaphenylenediamine, diphenylamine, the naphthylamines and their alkyl derivatives leads directly to the production of azo- derivatives ; in these cases, intermediate diazoamines have not been isolated, except when the reactive *ortho-* or *para-* positions are already substituted (Morgan, J.C.S. 1902, **81**, 91 ; 1907, **91**, 370).

When an aromatic base, XNH_2, is coupled with a diazonium salt, YN_2Cl, the resulting diazoamine is identical with that produced from XN_2Cl and YNH_2, and is generally regarded as being an equilibrium mixture of the two isomerides $XNH\cdot N_2Y$ and $XN_2\cdot NHY$. This explanation assumes the migration of the diazo-group which has been observed to occur in several instances (Griess, Ber. 1882, **15**, 2190 ; Schraube and Fritsch, 1896, **29**, 287 ; Hantzsch and F. M. Perkin, 1897, **30**, 1412).

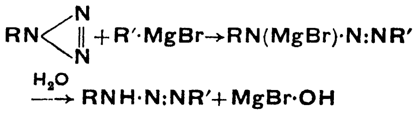
(For the constitution of the unsymmetrical aromatic diazoamines, $XNH\cdot N_2Y$, *v.* Meldola and Streatfeild, J.C.S. 1886, **49**, 624 ; 1887, **57**, 102, 434 ; 1886, **53**, 664 ; 1889, **55**, 412 ; 1890, **57**, 785 ; *cf.* Forster and Garland, *ibid.* 1909, **95**, 2051.)

Pyrolysis of Diazoamino benzene and -*p*-toluene.—In 1892 Hirsch pyrolysed diazoaminobenzene and obtained *p*-aminoazobenzene, diphenylamine, *ortho-* and *para*-aminodiphenyls (*o-* and *p*-xenylamines), aniline, benzene, and diphenyl with evolution of nitrogen. More recently azobenzene has been identified among these pyrolytic products.

A quantitative study of the pyrolysis of diazoamino-*p*-toluene dissolved in *p*-toluidine at 150° has shown that the more volatile products are nitrogen, ammonia, and toluene, whereas the less volatile products are azo-*p*-toluene, *p*-ditolylamine, 6-amino-3:6′-dimethylazobenzene and two isomeric aminoditolyls (15% yield). One isomeride obtained in very small amount has not been orientated ; the more plentiful isomeride is 4′:5-dimethyl-2-xenylamine, the oily triazo- compound of which is converted pyrogenically into 2:6-dimethylcarbazole (Morgan and Walls, J.C.S. 1930, 1502).

2. Aliphatic-Aromatic Diazoamines.

The diazoamines containing one aliphatic and one aromatic group can be produced by (1) coupling a diazonium salt with an aliphatic amine (Goldschmidt and Holm, Ber. 1888, **21**, 1016, 1112 ; Goldsmidt and Badl, 1889, **22**, 938 ; Bamberger and Müller, *ibid.* 1302) ; (2) treating an azide with Grignard reagent :



$$RN\left<\begin{matrix}N\\ \|\\ N\end{matrix}\right. + R'\cdot MgBr \rightarrow RN(MgBr)\cdot N{:}NR' \xrightarrow{H_2O} RNH\cdot N{:}NR' + MgBr\cdot OH$$

(Dimroth, Ber. 1903, **36**, 909 ; 1905, **38**, 670, 2328 ; 1907, **40**, 2390). Diazoamines present the possibility of stereoisomerism, but their relative stability and the fact that they couple only slowly with β-naphthol confirm the view that they are generally *anti*-diazo- compounds.

(For stereoisomeric diazoamines *v.* Orloff, J. Russ. Phys. Chem. Soc. 1906, **38**, 578 ; Vaubel, Z. angew. Chem. 1900, **13**, 762 ; 1902, **15**, 1209.)

Aromatic bisdiazoamino- compounds, *e.g.* $(C_6H_5\cdot N_2)_2N\cdot C_6H_5$, have been obtained by the action of two molecular proportions of a diazonium salt on one of an aromatic amine (Hantzsch, Ber. 1894, **27**, 1863; von Pechmann and Frobenius, 1895, **28**, 170).

Mixed aliphatic-aromatic bisdiazoamino- derivatives (*v.* Goldschmidt *et al.*, Ber. 1888, **21**, 1016 ; 1889, **22**, 933 ; 1907, **40**, 2390).

Diazo-ψ-semicarbazines (*v.* Forster, J.C.S. 1906, **89**, 223).

3. Aliphatic Diazoamines.

Dimroth's general method may be applied to the production of purely aliphatic diazoamino- compounds. In this way, the simplest member of the series, **diazoaminomethane (dimethyltriazene)**, $CH_3N{:}N\cdot NH\cdot CH_3$, has been prepared from methyl azide and magnesium methyl iodide. This substance, which is isolated by distilling its copper derivative with diazoaminobenzene under reduced pressure, is a colourless liquid, solidifying at −12° and boiling at 92° (Dimroth, Ber. 1905, **38**, 1575 ; 1906, **39**, 3905).

IV. Binuclear Diazo-oxides.

When a diazonium salt couples with a phenol the product is generally an *ortho-* or a *para-*hydroxyazo- compound (the C-azo- derivative), but in all probability, the O-azo- derivative is first produced, for in a few instances, when the velocity of transformation has been lessened by substitution, the intermediate O-azo- compound or diazo-oxide has been isolated. *p*-Bromobenzenediazonium chloride and *p*-nitrophenol give *p-bromobenzenediazo-4-oxynitrobenzene*

$$C_6H_4Br{\cdot}N{:}N{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$$

which, at 80°, becomes transformed into its isomeride, *p-bromobenzene-2-azo-4-nitrophenol*

$$C_6H_4BrN{:}N{\cdot}C_6H_4(NO_2)OH$$

(Dimroth and Hartmann, Ber. 1908, **41**, 4027; Auwers, *ibid.* 4304).

Occasionally traces of these intermediate diazoamines and diazo-oxides can be detected in the commercial azo- colouring matters (Vaubel, Z. Farben. Textil. Ind. 1902, **1**, 3).

V. Metallic Derivatives of Diazo-Compounds.

In 1894 Schraube and Schmidt (Ber. 1894, **27**, 514) found that on adding a 10% solution of *p*-nitrobenzenediazonium chloride to 18% aqueous sodium hydroxide at 50–60°, a sodium diazo- derivative separated in yellow bronzy leaflets, to which they gave the formula

$$NO_2{\cdot}C_6H_4{\cdot}NNa{\cdot}NO{,}H_2O,$$

regarding the compound as the *sodium* derivative of *p-nitrophenylnitrosamine.* This view of the constitution of the product was confirmed by the action on the compound of methyl iodide, when *p*-nitrophenylmethylnitrosamine,

$$NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}NO,$$

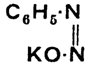
was obtained.

This sodium salt, which was regarded by Hantzsch as having the constitution of an anti-diazo- compound, **sodium *p*-nitrobenzenediazo-oxide** (*v. infra*), has been manufactured for use in the production of "nitrosamine red" (Badische Anilin- und Soda-Fabrik, G.P. 78874, 80263, 81134, 81202). The addition of excess of mineral acid to this metallic diazo- derivative determines the regeneration of the original diazonium salt, but treatment with dilute acetic acid leads to the formation of a yellow product, p-*nitrophenylnitrosamine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NO$, a substance showing little tendency to couple with β-naphthol.

The silver derivative obtained from the foregoing sodium salt yields on methylation an oxygen ether $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}O{\cdot}CH_3$, a reaction suggesting the possibility of tautomeric change. In many instances two isomeric modifications of these metallic diazo- derivatives have been isolated.

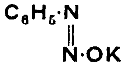
Benzenediazonium chloride and cold concentrated potassium hydroxide yield the normal *labile* form of *potassium benzenediazo-oxide* (I), which readily couples with β-naphthol. The *stable* modification of *potassium benzenediazo-oxide* (II) is produced by heating the strongly alkaline solution of the normal or labile salt at 130–140°; this isomeride couples only very slowly with β-naphthol.

According to Hantzsch, these isomerides have respectively the following formulæ :



$$\begin{matrix}C_6H_5{\cdot}N\\ \|\\ KO{\cdot}N\end{matrix}$$

I. *Syn*- (labile form).

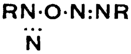


$$\begin{matrix}C_6H_5{\cdot}N\\ \|\\ N{\cdot}OK\end{matrix}$$

II. *Anti*- (stable form).

Dobbie and Tinkler (J.C.S. 1905, **87**, 273) have found, however, that these isomeric potassium salts have totally different ultra-violet absorption spectra. But as stereo-isomerides, like the benzaldoximes, have identical absorption spectra, it seems probable that the above isomeric salts are structurally dissimilar. Confirmation of the stereochemical theory would be obtained by isolating the *anti*-diazohydroxide from the stable (*anti-*) potassium salt, but on treating this with an acid, the nitrosamine separates. Moreover, the product supposed by Hantzsch and Pohl to be an *anti*-diazohydroxide (Ber. 1902, **35**, 2964) was shown by Orton to be a mixture of quinonediazide and a hydroxyazo- compound (Proc. Roy. Soc. 1903, **71**, 153 ; J.C.S. 1903, **83**, 796).

The existence of the *syn-* diazohydroxides is doubtful, and diazonium hydroxides (*v. supra*) are only known in solution.

Diazo-anhydrides, $RN{:}N{\cdot}O{\cdot}N{:}NR$ or  $\begin{matrix}RN{\cdot}O{\cdot}N{:}NR\\ \cdots\\ N\end{matrix}$, are very unstable explosive compounds produced by the action of acetic acid on the metallic *syn*-diazo-oxides. The *anti*-diazo-oxides, when thus treated, give nitrosamines.

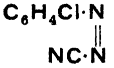
Aromatic diazoic acids, $Ar{\cdot}N_2O_2H$. Benzenediazoic acid, produced by oxidising potassium benzene*syn*diazo-oxide or -*iso*diazo-oxide with potassium ferricyanide in alkaline solution, is obtained in sparingly soluble white leaflets (m.p. 46°) dissolving readily in organic solvents or alkalis. With mineral acids it is transformed into *o-* and *p*-nitroaniline, and with hypochlorites it yields 4-chloro-2-nitroaniline. Its sodium salt gives the α- or N-ester, $C_6H_5{\cdot}N(CH_3){\cdot}NO_2$, the silver salt furnishes the β- or O-ester, $C_6H_5{\cdot}N{:}NOO{\cdot}CH_3$. Since the acid is also obtained by the action of nitrogen pentoxide on aniline it is probably a tautomeric substance :

$$C_6H_5{\cdot}NH{\cdot}NO_2 \rightleftharpoons C_6H_5{\cdot}N{:}NO_2H$$

(Bamberger, Ber. 1893, **26**, 471 ; 1894, **27**, 359 914, 584, 1273 ; Hantzsch, Ber. 1902, **35**, 258).

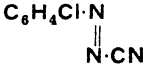
VI. Diazocyanides.

The addition of the calculated amount of potassium cyanide to a cold acid solution of a diazonium salt determines the formation of a sparingly soluble diazocyanide. In many instances, two modifications of the diazocyanides can be distinguished, and these varieties are regarded by Hantzsch as being stereoisomeric forms. *p*-Chlorobenzenediazonium chloride, from *p*-chloraniline, yields below −5° the yellow labile **syn-p-chlorobenzenediazocyanide** (I), which readily evolves nitrogen,



$$\begin{array}{r} C_6H_4Cl\cdot N \\ \| \\ NC\cdot N \end{array}$$

syn-Diazocyanide.
I.

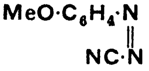


$$\begin{array}{l} C_6H_4Cl\cdot N \\ \quad\ \| \\ \quad\ N\cdot CN \end{array}$$

anti-Diazocyanide
II.

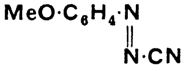
yields *p*-chlorobenzonitirile on treatment with copper powder, and readily passes into the stable **anti-p-chlorobenzenediazocyanide** (II). The latter substance, which is not affected by copper powder, may be distilled in steam without decomposition (Hantzsch and Schulze, Ber. 1895, **28**, 666).

Confirmation of this stereochemical theory of the constitution of the diazocyanides has been obtained by a study of the cyanides derived from *p*-methoxybenzenediazonium chloride. This salt with potassium cyanide in alcoholic solution yields the *syn*-diazocyanide (III), an orange-red insoluble substance (m.p. 51°), which couples with *β*-naphthol and slowly changes into the non-coupling *anti*-diazocyanide (IV), a brownish-red compound, melting at 121°.



$$\begin{array}{r} MeO\cdot C_6H_4\cdot N \\ \| \\ NC\cdot N \end{array}$$

III.



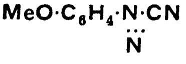
$$\begin{array}{l} MeO\cdot C_6H_4\cdot N \\ \qquad\qquad\ \| \\ \qquad\qquad\ N\cdot CN \end{array}$$

IV.

The existence of a third isomeric cyanide is indicated by evaporating at the ordinary temperature in the presence of excess of hydrocyanic acid, an aqueous solution of *p*-methoxybenzenediazonium hydroxide. The colourless crystalline product has the composition

$$MeO\cdot C_6H_4\cdot N_2\cdot CN,HCN,2H_2O$$

and possesses all the properties of a true metallic salt ; it is very soluble, and its solution is an electrolyte. Moreover, this double salt couples with *β*-naphthol and is converted by alkalis into the yellow *syn*-diazocyanide. These properties correspond with those of the normal diazonium salts, and the foregoing soluble cyanide is regarded as having the following constitution :



$$\begin{array}{l} MeO\cdot C_6H_4\cdot N\cdot CN \\ \qquad\qquad\ \vdots \\ \qquad\qquad\ N \end{array}$$

(Hantzsch, Ber. 1900, **33**, 2161 ; Euler and Hantzsch, 1901, **34**, 4166).

The two pairs of diazocyanides from *p*-chloraniline and *p*-anisidine were examined spectroscopically by Dobbie and Tinkler, who found that each pair gave almost identical ultra-violet absorption spectra, whereas the above soluble diazonium cyanide gave an entirely different spectrum. These results are in accordance with Hantzsch's view of the configuration of the diazo- and diazonium cyanides (J.C.S. 1905, **87**, 273).

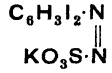
It has, however, been suggested by several workers in this field that the isomerism of the diazocyanides is structural, the *syn*- compounds being *iso*cyanides $R\cdot N:N\cdot NC$ and their *anti*-isomerides, cyanides $R\cdot N:N\cdot CN$ (Pechmann, Ber. 1895, **28**, 861 ; Orton, J.C.S. 1903, **83**, 805).

VII. Diazosulphonates.

Although the stereochemical theory of the constitution of diazocyanides is supported by physical as well as chemical evidence, yet it is significant that the only other series of salts in which this isomerism has been detected is one derived from sulphurous acid, a substance resembling hydrocyanic acid in giving rise to organic isomeric derivatives which are structurally dissimilar.

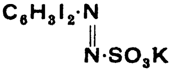
The diazosulphonates, prepared by adding potassium sulphite to aqueous solutions of benzenoid diazonium chlorides, frequently exist in two differently coloured modifications, but in most cases the *syn*- isomeride is too unstable to be isolated in a pure state.

Potassium syn-2:4-diiodobenzenediazosulphonate (I) is an orange substance, whilst the *anti*- salt (II) is yellow :



$$\begin{array}{r} C_6H_3I_2\cdot N \\ \| \\ KO_3S\cdot N \end{array}$$

I.



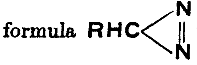
$$\begin{array}{l} C_6H_3I_2\cdot N \\ \qquad\ \| \\ \qquad\ N\cdot SO_3K \end{array}$$

II.

The diazotised naphthylamines behave exceptionally, yielding only *syn*-diazosulphonates, which, on warming, pass, not into their *anti*-isomerides, but into the corresponding azonaphthalenes (Hantzsch and Schmiedel, Ber. 1897, **30**, 71).

The *syn*- and *anti*- modifications of **potassium benzenediazosulphonate**, $C_6H_5\cdot N:N\cdot SO_3K$, were found by Dobbie and Tinkler (*l.c.*) to have identical ultra-violet absorption spectra. This fact supports the stereochemical theory of their structures (*cf.* Hantzsch, Ber. 1894, **27**, 1726, 2099, 2586 ; Bamberger, *ibid.* 2930, 3527 ; Bamberger, Ber. 1895, **28**, 225, 444, 826 ; Pechmann, *ibid.* 861 ; Claus, J. pr. Chem. 1894, [ii], **50**, 239 ; Meyer and Jacobsen, Lehrbuch der Org. Chem. 1902, ii, 303).

VIII. Aliphatic Diazo- Compounds.

The amines of the aliphatic series, when treated with nitrous acid, generally lose their basic nitrogen, the amino- group becoming replaced by hydroxyl. In some cases, however, the nitrogen is retained and an aliphatic diazo-compound is produced, having the general formula  $RHC\!<\!\begin{array}{c}N\\ \|\\ N\end{array}$ with the azo- group attached entirely to the same carbon atom.

An alternative formulation has been suggested for the aliphatic diazo- compounds in which one nitrogen is quinquevalent, so that the general formula becomes $:>C:N\,\vdots\,N$ (Thiele, Ber. 1911, **44**, 2522 ; Forster and Cardwell, J.C.S. 1913, **103**, 861 ; *cf.* Ber. 1912, **45**, 1654 ; 1916, **49**, 1884.

Although glycine is converted by nitrous acid or alkyl nitrites into glycollic acid, yet its ethyl ester gives rise to **ethyl diazoacetate**, $N_2{:}CH{\cdot}CO_2{\cdot}C_2H_5$, a yellow liquid freezing at −22° and boiling at 143–144°/721 mm. (Curtius, Ber. 1883, **16**, 2230).

One kg. of ethyl aminoacetate hydrochloride and 750 g. of sodium nitrite are added successively to 2 litres of water containing 5 g. of sodium acetate. The mixture is shaken until the temperature falls to 0° ; 5 c.c. of 10% sulphuric acid and 500 c.c. of ether are added and the liquids thoroughly agitated. The ethereal layer is separated and the treatment with dilute acid and ether repeated until red fumes are evolved. The ethereal extracts are washed with dilute aqueous sodium carbonate till alkaline, dried with calcium chloride, and the solvent removed on the water-bath. The yield of ethyl diazoacetate is 94·7% of the calculated quantity (Silberrad, J.C.S. 1902, **81**, 600).

With iodine, ethyl diazoacetate yields diiodoacetic acid, and with aldehydes it condenses to form ketonic esters :

$$R{\cdot}CHO+N_2{:}CH{\cdot}CO_2{\cdot}C_2H_5 \rightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$$

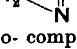
One of the most remarkable reactions of this diazo- ester is its condensation with benzene and its homologues, giving rise to a series of esters containing seven-membered hydrocarbon rings (Buchner, Ber. 1896–1903, **29**, 106 ; **30**, 632, 1949 ; **31**, 399, 402, 2004, 2241, 2247 ; **32**, 705 ; **33**, 184 ; **36**, 3509 ; Annalen, 1908, **358**, 1).

Ethyl diazoacetate when heated with alkalis undergoes a series of complex polymeric changes (Curtius, Ber. 1885, **18**, 1283 ; 1906, **39**, 1383, 3398, 4140 ; 1907, **40**, 84, 815, 1176, 1194, 1470 ; 1908, **41**, 3116, 3140, 3161 ; J. pr. Chem. 1888, [ii], **38**, 408 ; Hantzsch, Ber. 1900, **33**, 58 ; *cf.* Silberrad, J.C.S. 1902, **81**, 598).

Diazo- derivatives are not obtained from free α-amino-carboxylic acids, and only from those amino-esters of aliphatic acids containing the amino- group in the α-position with respect to the alkylated carboxyl group. The esters of those polypeptides which contain the amino-group in the α-position to a carbimino group can also be transformed into diazo- derivatives.

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et \rightarrow N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$$

The α-aminoketones (*e.g.* α-aminoacetophenone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}NH_2$) give diazo- compounds (Angeli, Ber. 1904, **37**, 2080), and so also do certain uric acid compounds, *e.g.* aminomethyluracil.



Diazomethane, $CH_2\langle\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$ or $CH_2{:}N{:}N$, the simplest aliphatic diazo- compound, is prepared by adding methyl-alcoholic potassium hydroxide to an ethereal solution of nitrosomethylurethane,

$$C_2H_5{\cdot}O{\cdot}CO{\cdot}N(CH_3){\cdot}NO,$$

and distilling the mixture on the water-bath, when the distillate consists of an ethereal solution of the diazo- compound, the yield being 50% of the calculated quantity. This substance is also produced by the action of hydroxylamine on methyldichloramine :

$$CH_3{\cdot}NCl_2+H_2NOH=CH_2{:}N_2+H_2O+2HCl$$

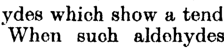
Diazomethane is a poisonous yellow gas condensing to a yellow liquid boiling at −24° to −23° and solidifying in pale yellow crystals melting at −145°. It is a powerful methylating agent, converting hydroxyl groups into methoxyl, and alkylating primary and secondary bases. With iodine, diazomethane gives nitrogen and methylene iodide, and aldehydes are converted into methyl ketones (*cf.* Meyer, Monatsh. 1905, **26**, 1295, 1311 ; Acree, Johnson, Brunel, Shadinger and Nirdlinger, Ber. 1908, **41**, 3199 ; Schlotterbeck, Ber. 1907, **40**, 479; 1909, **42**, 2559 ; Forster and Holmes, J.C.S. 1908, **93**, 242).

Diazomethane combines additively with unsaturated compounds ; with acetylene it gives pyrazole (von Pechmann, Ber. 1898, **31**, 2950), and with ethyl fumarate it furnishes ethyl pyrazolinecarboxylate.

Diazomethane reacts with certain aldehydes, forming methyl ketones :

$$R{\cdot}CHO+CH_2N_2=R{\cdot}CO{\cdot}CH_3+N_2$$

There is an alternative reaction exhibited by those aldehydes which show a tendency to form hydrates. When such aldehydes react with diazomethane, substituted ethylene oxides are formed. *p*-Nitrobenzaldehyde gives a mixture of *p*-nitroacetophenone and *p*-nitrophenylethylene oxide,



$$NO_2{\cdot}C_6H_4{\cdot}\underbrace{CH{\cdot}CH_2}_{O}$$

Similarly chloral is converted into

ααα-trichloropropylene-βγ-oxide, $CCl_3{\cdot}\underbrace{CH{\cdot}CH_2}_{O}$

(Arndt and Eistert, Ber. 1928, **61**, [B], 1118, with Amende, *ibid.* 1949).

A similar process occurs when acid chlorides treated with diazomethane yield either diazoketones or chloroketones. In the former alternative the acid chloride (1 mol.) is added to an ethereal solution of diazomethane (2 mols.) :

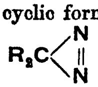
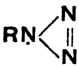
$$R{\cdot}COCl+CH_2N_2=R{\cdot}CO{\cdot}CHN_2+HCl$$

The hydrogen chloride liberated decomposes any excess of diazomethane ; it also attacks the diazoketone so that the corresponding chloroketone may be prepared by the following reaction :

$$R{\cdot}CO{\cdot}CHN_2+HCl=R{\cdot}CO{\cdot}CH_2Cl+N_2$$

(Bradley and Robinson, J.C.S. 1928, 1310, 1545, 2904 ; Arndt and Amende, Ber. 1928, **61**, [B], 1122).

Although for some time open-chain formulæ have been adopted for aliphatic diazo- compounds $R_2C{=}N \overset{-}{\rightarrow} N$ and azides $R{\cdot}N{=}N \overset{-}{\rightarrow} N$, there is no really convincing evidence for these formulations. An examination of the electron-diffraction pattern of the vapour of diazomethane suggests that the compound is in resonance between the two phases $H_2C{=}\overset{+}{N}{=}\overset{-}{N}$ and $H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N$. Azomethane when similarly examined indicates the conventional formula $CH_3{\cdot}N{=}N{\cdot}CH_3$, but with methyl groups in the *trans-* positions (Boersch, Monatsh. 1935, 65, 311). Determinations of the parachors of certain azides made by Lindemann and Thiele (Ber. 1928, **61**, [B], 1529) are in favour of the cyclic arrangement, as is also the evidence derived from dipole moments.

Further support for the older cyclic formulæ for aliphatic diazo- compounds  and azides  is obtained from consideration of the boiling-points of many of these derivatives, which, if cyclic, should approximate to the boiling-points of the corresponding halides, whereas an open-chain structure would require boiling-points near those of the nitro-compounds. Actually the boiling-points of the azides lie near those of the bromides or between these and the boiling-points of the iodides (*cf.* Forster and Newman, J.C.S. 1910, **97**, 2572), whereas the boiling-points of the aliphatic diazo- compounds lie very near to those of the chlorides ; those of the nitro- compounds are always much higher (Sidgwick, J.C.S. 1929, 1108 ; Hantzsch, Ber. 1933, **66**, [B], 1349).

Diazoethane, $CH_3{\cdot}CH{:}N_2$, and **phenyldiazomethane**, $C_6H_5{\cdot}CH{:}N_2$, have both been prepared (Hantzsch and Lehmann, Ber. 1902, **35**, 897). The former closely resembles diazomethane, the latter is a dark-red oil.

Substitution increases considerably the colour of these diazo- derivatives : dimethyldiazomethane, $C(CH_3)_2{:}N_2$, is red and diphenyldiazomethane is obtained in bluish-red needles melting at 20° (Staudinger, Ber. 1916, **49**, 1884).

Diazomethane should not be confused with **azomethane**, $CH_3{\cdot}N{:}H{\cdot}CH_3$, the simplest azo-compound, which is produced by oxidising symmetrical dimethylhydrazine (hydrazomethane) with chromic acid (Thiele, Ber. 1909, **42**, 2575). Azomethane is a colourless gas condensing to a pale yellow liquid (b.p. 1·5°).

Diazomethanedisulphonic acid, a noteworthy example of an aliphatic diazo-compound, results from the interaction of potassium cyanide and potassium bisulphite in presence of caustic potash. The solution, acidified and treated with nitrous acid, yields successively aminomethanedisulphonic acid and the diazo- compound. Sulphurous acid and diazomethanedisulphonic acid yield an additive compound which, on boiling, furnishes hydrazine (von Pechmann, Ber. 1895, **28**, 2374 ; 1896, **29**, 2161).

Diazoacetone, $CH_3{\cdot}CO{\cdot}CH{:}N_2$, a pale yellow liquid, is obtained from aminoacetylacetone by converting this base into diazoacetylacetone anhydride and treating this product with aqueous caustic alkali (Wolff, Annalen, 1912, **394**, 23).

Metallic diazo- derivatives of the aliphatic series are produced by treating nitroso-alkyl urethanes with concentrated caustic potash solution or ethereal potassium ethoxide. **Potassium methyldiazo-oxide**,

$$CH_3{\cdot}N{:}N{\cdot}OK,H_2O,$$

separates in white crystals, when nitrosomethylurethane is added to concentrated aqueous caustic potash at 0°. **Potassium benzyldiazo-oxide**, $C_6H_5{\cdot}CH_2{\cdot}N{:}N{\cdot}OK,H_2O$, is similarly prepared from nitrosobenzylurethane. These metallic derivatives are very unstable ; they are decomposed by water with explosive violence, yielding respectively diazomethane and phenyldiazomethane (Hantzsch and Lehmann, Ber. 1902, **35**, 897).

Bibliography.—Hantzsch, " Die Diazoverbindungen, Ahren's Sammlung, Chemischer und Chemisch-technischer Vorträge," 1902 ; Morgan, " Our Present Knowledge of Aromatic Diazo-Compounds," Brit. Assoc. Report, 1902 ; Eibner, " Zur Geschichte der Aromatischen Diazoverbindungen," 1903 ; Cain, " The Chemistry and Technology of the Diazo- Compounds," 1920 ; Saunders, " The Aromatic Diazo- Compounds and their Technical Applications," 1936.

G. T. M.

DIAZODINITROPHENOL (**4:6-dinitro-2-diazophenol**). This example of the non-metallic explosive primer has been patented by W. M. Dehn (U.S.P. 1404687), who claimed that it is suitable for general priming purposes, especially where fouling and amalgamation with metals are to be avoided. It is stated to be non-hygroscopic and can be stored under water at ordinary temperatures for months without undergoing any appreciable change. It is stable in contact with cold mineral acids but is decomposed by alkalis. Diazodinitrophenol can be safely and strongly compressed without its explosive power being impaired. When heated above 150°C., it explodes violently, but if finely divided and wetted with water it cannot be detonated by means of a No. 8 cap. Diazodinitrophenol is more powerful than fulminate of mercury and when mixed with potassium chlorate in suitable proportions exhibits about 40% more energy on detonation than the most efficient mixtures of fulminate and chlorate.

H.S.

DIAZOTYPE PAPER *v.* DIAZO- COMPOUNDS (this vol. p. 590*a*).

***o-o′*-DIBENZIL**,

$$PhCO{\cdot}CO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}COPh,$$

for method of preparation, *see* Zincke and Tropp (Annalen, 1908, **363**, 302).

DIBROMIN, 5:5-dibromodiallylbarbituric acid (*v.* BARBITURIC ACID, Vol. I, p. 623).

DICARBOXYLIC ACIDS, Higher Aliphatic. There are three general synthetic processes for the production of these compounds :

(i) The electrolysis of the potassium salts of the half-esters of lower dicarboxylic acids :

$$2CO_2Et{\cdot}[CH_2]_n{\cdot}CO_2K \rightarrow CO_2Et{\cdot}[CH_2]_{2n}{\cdot}CO_2Et$$

(Crum Brown and Walker, Annalen, 1891, **261**, 123 ; Walker and Lumsden, J.C.S. 1901, **79**, 1200 ; Carmichael, *ibid.* 1922, **121**, 2545 ; Fairweather, Proc. Roy. Soc. Edin. 1926, **46**, 71).

(ii) Condensation of the appropriate dihalide with potassium cyanide, followed by hydrolysis :

$$Br{\cdot}[CH_2]_n{\cdot}Br \xrightarrow{KCN} CN{\cdot}[CH_2]_n{\cdot}CN \xrightarrow{\text{hydrol.}} CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$$

(von Braun, Ber. 1909, **42**, 4550 ; von Braun and Danziger, *ibid.* 1912, **45**, 1975).

(iii) Condensation of the appropriate dihalide with ethyl sodiomalonate, followed by hydrolysis and decarboxylation, *e.g.* :

$$
\begin{aligned}
&Br{\cdot}[CH_2]_n{\cdot}Br \\
&\quad\longrightarrow (CO_2Et)_2{\cdot}CH{\cdot}[CH_2]_n{\cdot}CH(CO_2Et)_2 \\
&\qquad\qquad\longrightarrow CO_2H{\cdot}[CH_2]_{n+2}{\cdot}CO_2H
\end{aligned}
$$

(Franke and Hankam, Monatsh. 1910, **31**, 188 ; Chuit, Helv. Chim. Acta, 1926, **9**, 264 ; 1927, **10**, 167).

The dihalides necessary for procedures (ii) and (iii) may be obtained from a lower dibasic acid by the following series of operations :

$$
\begin{aligned}
&CO_2Et{\cdot}[CH_2]_n{\cdot}CO_2Et \\
&\quad\xrightarrow{\text{reduction}} OH{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OH \\
&\qquad\qquad\qquad\qquad \big\downarrow{\scriptstyle HBr} \\
&\qquad\qquad\qquad Br{\cdot}[CH_2]_{n+2}{\cdot}Br
\end{aligned}
$$

If desired, two more methylene groups may be introduced into the chain, thus :

$$
\begin{aligned}
&Br{\cdot}[CH_2]_n{\cdot}Br \xrightarrow{Mg} BrMg[CH_2]_nMgBr \\
&\qquad\qquad\qquad\qquad \big\downarrow{\scriptstyle CH_2Cl{\cdot}OMe} \\
&\qquad MeO{\cdot}CH_2{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}OMe \\
&\qquad\qquad\qquad\qquad \big\downarrow{\scriptstyle HBr} \\
&\qquad\qquad\quad Br{\cdot}[CH_2]_{n+2}{\cdot}Br
\end{aligned}
$$

(Chuit, *l.c.*).

Certain of these acids occur naturally ; thus, tetradecane-1:14-dicarboxylic acid (thapsic acid), $CO_2H{\cdot}[CH_2]_{14}{\cdot}CO_2H$, occurs, in combination, in the roots of *Thapsia garganica* L. (Canzoneri, Gazzetta, 1883, **13**, 514) and as a glyceride in the wax of *Juniperus Sabina* (Bougault, Compt. rend. 1910, **150**, 875), and heptadecane-1:17-, octadecane-1:18-, and nonadecane-1:19- dicarboxylic acids as glycerides in Japan wax (Geitel and van der Want, J. pr. Chem. 1900, [ii], **61**, 153 ; Schaal, Ber. 1907, **40**, 4785 ; Ruzicka, Stoll and Schinz, Helv. Chim. Acta, 1928, **11**, 670).

The chief interest of these compounds lies, however, in their conversion into ketones by distillation of their thorium salts ; the large-ring ketones so obtained are useful in perfumery as fixatives, *cyclo*pentadecanone (*exaltone*) being particularly valuable in this respect. For a general review of this subject, *see* Ruzicka, Chem. and Ind. 1935, **54**, 2.

The melting-points of the best-known straight-chain higher dicarboxylic acids,

$$CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H,$$

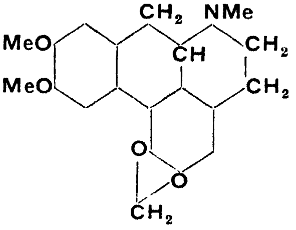
are given in the following table :

n.	9	10	11	12	13	14	15	16
m.p.	110°	128°	113°	126°	115°	124°	118°	125°

n.	17	19	20	21	24	28	32
m.p.	119°	112°	124°	118°	124°	123°	123°

H. N. R.

DICENTRINE, $C_{20}H_{21}O_4N$, an alkaloid occurring in various *Dicentra* species, first isolated by Heyl from *D. formosa* (0·1%) (Arch. Pharm. 1903, **241**, 313), later by Asahina from *D. pusilla* (0·14–0·35%) and *D. spectabilis* (Arch. Pharm. 1909, **247**, 201) and by Manske from *D. oregana* and *D. eximia* (0·31%) (Canad. J. Res. 1933, **8**, 592 ; 1934, **10**, 765). It crystallises from Et_2O,EtOH or $CH_3{\cdot}CO_2Et$ in prisms, m.p. 168–169°, $[\alpha]_D$ +62·1° (in chloroform). The salts are well crystallised, characteristic is dicentrine-methine, m.p. 158–159° (Manske *l.c.* ; Ghose, Krishna, and Schlittler, Helv. Chim. Acta, 1934, **17**, 919). Absorption spectrum, *see* Girardet (J.C.S. 1931, 2630) and Kitasato (A. 1927, 1094). Gadamer, for theoretical reasons, assigned the following constitution to dicentrine (Arch. Pharm. 1911, **249**, 698)—



Dicentrine.

which was found to be correct by synthesis (Haworth, Perkin and Rankin, J.C.S. 1925, 2018; 1926, 29).

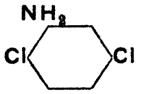
Osada (Amer. Chem. Abstr. 1928, **22**, 3664) by splitting off from dicentrine the methylenedioxy- group with phloroglucinol-H_2SO_4 and completely methylating the phenolic base obtained glaucine. Dicentrine was obtained by methylating the phenolic alkaloid actinodaphnine (Ghose, Krishna, and Schlittler, *l.c.*).

According to Iwakawa (Arch. exp. Path. Pharm. 1911, **64**, 369) dicentrine in small doses produces narcosis, in large doses it causes convulsions, attacks the heart, and paralyses the respiratory centres.

Schl.

DICHLORAMINE T, toluene-*p*-sulphondichloramide, $C_6H_4Me{\cdot}SO_2{\cdot}NCl_2$, is produced by treating toluene with chlorsulphonic acid, converting the sulphonic chloride thus obtained into the amide which is then chlorinated (*see* T. Aldoschin, G. Chimici, 1934, **28**, 87). Under many trade names it is now of great importance in many fields, *e.g.* as a disinfectant (R. Dietzel, Arch. Pharm. 1928, **266**, 123 ; D.R.P. 401011 ; Dan. P. 49704, etc.), as a bleaching agent in the textile industry (H. Tatu, Rev. gén. Teinture, 1933, **11**, 883), as a disinfectant for agricultural purposes (U.S.P. 2002589), as an oxidising and chlorinating agent (A. Bradfield, J.C.S. 1928, 782 ; J. Koetschet, Helv. Chim. Acta, 1930, **13**, 587 ; G. Schiemann, Z. angew. Chem. 1927, **40**, 1032), etc.

2:5-**DICHLOROANILINE**,



is prepared by reducing the corresponding nitro-compound with tin and acid (Jungfleisch, Ann.

Chim. 1868, [iv], **15**, 259) with nickel and hydrogen (F.P. 621434) or by chlorination and subsequent hydrolysis of 3-chloroacetanilide (Beilstein and Kurbatow, Annalen, 1879, **196**, 215, 220). For preparation, *see* M. Kohn and S. Fink, Monatsh. 1931, **58**, 73).

2:5-Dichloroaniline has m.p. 50°, b.p. 250°. It undergoes the normal Skraup reaction to give 5:8-dichloroquinoline (F.P. 727528), but is more valuable as the first component of a variety of azo- dyestuffs (G.P. 112820, 193211, 251843, 256999; B.P. 329353, etc.), and others which, whilst not true azo- dyestuffs, yet employ 2:5-dichlorodiazobenzene salts as intermediates (G.P. 460087, B.P. 314899). It yields 2:5-*dichloroaniline*-4-*sulphonic acid* on sulphonation with fuming sulphuric acid at 170–180°, this is oxidised by potassium dichromate to 2:5-*dichloroquinone* (Noelting and Kopp, Ber. 1905, **38**, 3513), and on diazotisation affords the diazoanhydride (Battegay, Ber. 1906, **39**, 84), which yields azo- dyestuffs (G.P. 222991, 268599, 273934).

DICHROITE, a silicate of aluminium and magnesium with some ferrous iron replacing magnesium.

DICINCHONICINE (**DICINCHONINE**) *v.* Cinchona Alkaloids, this vol. p. 161*d*.

DI-CITURIN. Trade name for the monopotassium salt of diacetylcitric acid (*Paynes and Byrne, London*), B.P.C. 1934.

DICKITE. A crystallised clay mineral, $H_4Al_2Si_2O_8$, differing slightly from kaolinite in its optical characters and X-ray pattern. The minute crystals from Almwch in Anglesey were first described as kaolinite by A. B. Dick in 1888.

L. J. S.

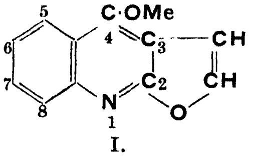
DICONQUININE *v.* Cinchona Alkaloids, this vol., p. 162*a*.

DICROTYL, $\Delta^{\beta\zeta}$-*octadiene*, *v.* Butadienes and Polyolefins (non-conjugated).

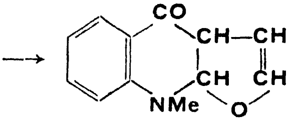
DICTAMNINE, $C_{12}H_9O_2N$, occurs in *Dictamnus albus* (white dittany; Fr. *dictame blanc*, Ger. *Weisser Diptam*), which belongs to the Rutaceæ. It was first isolated by Thoms (Ber. Deut. pharm. Ges. 1923, **33**, 68; Arch. Pharm. 1930, **268**, 39) (yield 0·3%), and later by Asahina, Ohta and Inubuse (Ber. 1930, **63**, [B], 2045) from *Skimmia repens* Nakai (yield 0·2%). For extraction, *see* Asahina *et al.* (*l.c.*).

It forms colourless prisms, m.p. 132–133°, and is an optically inactive, unsaturated weak base, insol. H_2O, sol. warm $EtOH$ and $CHCl_3$, less in Et_2O and $CH_3{\cdot}CO_2Et$; yields sparingly soluble chromate, picronolate m.p. 178°, chloroaurate, chloroplatinate, and picrate m.p. 163°. The hydrochloride, m.p. 170° (decomp.), hydrolyses in hot H_2O and the free base separates.

When treated with methyliodide in a sealed tube, dictamnine (I) is converted into *iso*-dictamnine (II), which contains $-NMe$ instead of $-OMe$, a reaction characteristic of α- and γ-methoxyquinolines. By oxidation and decarboxylation Asahina *et al.* (*l.c.*) finally obtained 2:4-dihydroxyquinoline, which makes the following formulæ probable:



I.



II.

An isomeric *pseudo*-dictamnine was synthesised by Asahina and Inubuse (Ber. 1932, **65**, [B], 61). For physiological action of dictamnine, *see* Thoms and Asahina.

Thoms (A. 1930, 383) further isolated from *D. albus*: *dictamnolactone*, $C_{16}H_{18}O_5$, m.p. 279–280°; *fraxinellone*, $C_{14}H_{16}O_3$, m.p. 117°, $[\alpha]_D^{15}$ −38·39°; *trigonelline* and *choline*. For dictamnic acid and dictamnal, *see* Asahina *et al.* (*l.c.*). *Skimmianine*, $C_{14}H_{13}O_4N$, was isolated from the leaves of *S. japonica* Thunb. (yield 0·06%) by Honda (Arch. exp. Path. Pharm. 1904, **52**, 68). The close relationship to dictamnine was suggested by the great similarity of the absorption spectra. The alkaloid, a weak base, crystallises in prisms, m.p. 176°, salts hydrolyse in H_2O, picrate, m.p. 195–197° (decomp.). It contains three OMe groups and, like dictamnine, is converted by methyliodide into *iso*skimmianine. Asahina and Inubuse (Ber. 1930, **63**, [B] 2052) consider that skimmianine is 7-8-dimethoxydictamnine.

From *Orixa japonica* Terasaka isolated four alkaloids (Amer. Chem. Abstr. 1932, **26**, 730; 1935, **29**, 7337):

Orixine, $C_{18}H_{23}O_6N$ or $C_{18}H_{21}O_6N$, $[\alpha]_D^{17}$ +83·29°, m.p. 152·5°.

Kokusagine, $C_{13}H_9O_4N$, optically inactive, m.p. 201°.

Kokusaginine, $C_{14}H_{13}O_4N$ or $C_{14}H_{15}O_4N$, m.p. 171°.

Kokusaginoline, $C_{17}H_{13}O_5N\cdot 1\frac{1}{2}H_2O$, m.p. 283°.

The properties of these four new alkaloids are very similar to those of dictamnine and skimmianine; the similarity also of the absorption-spectra is striking. Probably all contain the same heterocyclic ring-system. Terasaka supposes kokusagine to be 6:7-methylenedioxy-dictamnine.

Schl.

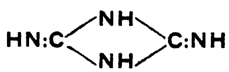
DICTAMNOLACTONE *v.* Dictamnine.

DICYANINE *v.* Cyanine Dyes.

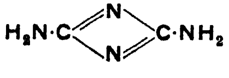
DICYANODIAMIDE, $(H_2CN_2)_2$, or cyanoguanidine. Obtained by polymerisation of cyanamide or, more conveniently, from commercial calcium cyanamide ("Kalkstickstoff"). The polymerisation is facilitated by addition of small amounts of acid, insufficient to combine with all the calcium present, and by boiling for a few hours. From the filtered extract dicyanodiamide crystallises in colourless needles, m.p. 205°. On heating sodium cyanamide with ammonium sulphate on a water bath cyanamide separates as an oil and on stirring or shaking polymerises in a few hours (Hermann, Monatsh. 1905, **26**, 1025). The rate of polymerisation is dependent on the reaction of the solution used and is greatest at p_H 9·6, decreasing rapidly above and below this point (Buchanan and Barsky, J. Amer. Chem. Soc. 1930, **52**, 195). On warming with dilute acid dicyanodiamide is converted into dicyanodiamidine (guanyl urea),

$$NH_2(NH:)C·NH·CO·NH_2,$$

which forms a characteristic insoluble compound with nickel, $Ni(C_2H_5N_4O)_2$ (Grossmann and Schück, Analyst, 1910, **35**, 247 ; 1909, **34**, 455 ; 1907, **32**, 273, 394). This reaction has been utilised in the determination of nickel in the presence of cobalt (cobalt dicyanodiamidine is soluble in water). The nickel compound can be dried at 115–160° without decomposition. C. D. Garby (Ind. Eng. Chem. 1925, **17**, 266) has adapted the reaction to the determination of dicyanodiamide, this is first converted to the -amidine, which is then precipitated as the nickel compound. Dicyanodiamide may also be determined as the insoluble compound with silver picrate (Johnson, J.S.C.I. 1921, **40**, 125T). Reduction of dicyanodiamide with zinc and dilute hydrochloric acid yields guanidine (dicyanodiamidine probably being formed intermedially (J. Bell, Sci. Proc. Roy. Dublin Soc. 1926, **18**, 207)), and hydrocyanic acid which is rapidly reduced to the further stage of methylamine (Bamberger and Seeberger, Ber. 1893 1583). Dicyanodiamide, on treatment with a mixture of nitric and sulphuric acid is converted into nitrodicyanodiamidine, and heating with ammonium salts (chloride, nitrate, or thiocyanate) yields guanidine salts (Werner and Bell, J.C.S. 1920, **117**, 1133 ; Ewan and Young, J.S.C.I. 1921, **40**, 109), probably by intermediate formation of diguanide salts. Condensation with dialkyl cyanacetic or malonic esters produces pyrimidine derivatives, *e.g.* with ethyl diethylcyanacetate a condensation product is obtained which on treatment with sulphuric acid gives barbituric acid (Bayer & Co., G.P. 165223 ; Chem. Zentr. 1906, **1**, 514). On autoclaving dicyanodiamide with liquid ammonia at 150° an 80% yield of, *melamine*, $C_3N_3(NH_2)_3$, is obtained. With ammonium carbonate, carbon dioxide, and water under similar conditions, 75% of melamine and 25% of guanidine carbonate are formed (W. Scholl *et al.*, Ind. Eng. Chem. 1937, **29**, 202). Condensation with formaldehyde in the presence of acid yields an artificial resin (F.P. 665210) which on addition of casein forms plastic moulding composition (B.P. 323047, 1927). The constitutional formula of dicyanodiamide has been variously described as $NH_2(NH:)C·NH·C:N$, $(NH_2)_2C:N·C:N$ (Bamberger, Ber. 1883, **16**, 1459 ; 1891, **24**, 899 ; Pohl, J. pr. Chem. 1908, [ii], **77**, 533 ; Prianischnikoff, J.S.C.I. 1909, **28**, 724) and more recently as the Baumann formula :



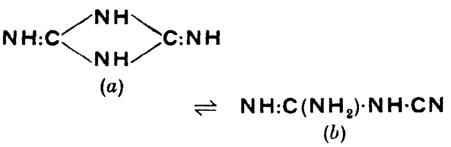
or



F. Chastellain (Helv. Chim. Acta, 1935, **18**, 1287) after a detailed study of the chain of reactions

$$\text{dicyanodiamide} \xrightarrow{\text{acid}} \text{dicyanodiamidine} \longrightarrow \text{guanidine} \xrightarrow{\text{NaOH at }100°} \text{urea} \longrightarrow \text{ammonia}$$

concludes that dicyanodiamide is a tautomeric compound :



and that in neutral and alkaline solutions and probably in the solid form it has the structure (*a*), whereas in acid solution this is transformed into (*b*).

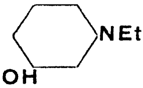
The commercial fertiliser calcium cyanamide usually contains small amounts of dicyanodiamide which was formerly supposed to be the cause of seedling losses sometimes observed when the fertiliser was applied at or within a few days of sowing (Cowie, J. Agric. Sci. 1918, **9**, 113). This is now known to be a fallacy (Lefort des Ylouses, Chim. et Ind. 1927, **18**, 216). Moreover, the amount of dicyanodiamide in modern forms of calcium cyanamide is extremely small.

A. G. Po.

DIDIAL. Trade name for a preparation containing dial and ethylmorphine diallylbarbiturate, administered as a powerful hypnotic (*Ciba, London*). B.P.C. 1934.

"DIENE SYNTHESIS" *v.* ALIZARIN AND ALLIED COLOURING MATTER, Vol. I, p. 208.

***m*-DIETHYLAMINOPHENOL,**



m.p. 78°, b.p. 201°/25 mm. is best made by sulphonation of diethylaniline followed by alkali fusion of the *m*-sulphonic acid (D.R.P. 44792, U.S.P. 403678 ; for a review of other methods, *see* Sansome, Rev. Gén. Mat. Col. 1924, **28**, 127).

m-Diethylaminophenol readily undergoes condensation with many compounds ; 1-2-dicarboxylic acids (*e.g.* itaconic, citraconic, succinic, etc.) give rhodamine dyestuffs, Rhodamine B (Brilliant Rose B) being the derivative of phthalic acid. It is a source of triphenylmethane dyes (D.R.P. 205758, 229466), oxazine dyes (D.R.P. 300253), and many others, and is used as an anti-oxidant in rubber technology (U.S.P. 1899120).

DIETHYLANILINE, $C_6H_5·NEt_2$, is produced by the classical methods of ethylation applied to aniline halogen hydrides ; by treatment of aniline with diethyl sulphate in presence of lime (U.S.P. 1570203), with alcohol and sulphuric acid (Laptew, Anilin Farb. Ind. (Russ.), 1934, **4**, 551), with ethyl chloride and lime under pressure (U.S.P. 1923697, 1994851), with ether under pressure (F.P. 768142), paraldehyde under pressure (F.P. 776613), etc. The simultaneous reduction and ethylation of nitrobenzene with zinc and acetaldehyde (D.R.P. 491856) and many catalytic processes employing alcohol as the ethylating agent (Brown and Reid, J. Amer. Chem. Soc. 1924, **46**, 1836; Roy, J. Indian Chem. Soc. 1928, **5**, 383; F.P. 669824) are of particular interest. A variety of methods employing chlorsulphonic acid (B.P. 270930), phosgene (B.P. 273923), phthalic acid (U.S.P. 1890246), maleic anhydride (U.S.P. 1991787), etc., are available for the removal of partially alkylated by-products. Diethylaniline has m.p. −81°, b.p. 216·5°.

Diethylaniline is characterised by its quaternary addition compound with benzyl chloride (m.p. 104°) (Marvel and co-workers, J. Amer. Chem. Soc. 1929, **51**, 3638) and is recommended as a reagent for aluminium (Grosset, Ann. Soc. sci. Bruxelles, 1933, [B], **53**, 16) and zinc (Eegriwe, Z. anal. Chem. 1928, **74**, 225).

Diethylaniline is used in the preparation of diphenylmethane derivatives (U.S.P. 1954484, 1803331) of azo dyestuffs and of dyestuffs belonging to the triphenylmethane and safranine series (F.P. 755338), etc. It also finds application in the treatment of lubricating oils (F.P. 636332) and as an anti-oxidant in rubber chemistry (D.R.P. 345160).

DIETZEITE. A double iodate and chromate of calcium crystallising in the monoclinic system, discovered in 1891 in the sodium nitrate deposits of Atacama, Chile. Analyses lead to the formula $7Ca(IO_3)_2 \cdot 8CaCrO_4$, but the simple double salt formula $Ca(IO_3)_2 \cdot CaCrO_4$ appears more probable. Distinct crystals are rare, the mineral usually forming crystalline fibrous aggregates of a dark gold-yellow colour. Sp.gr. 3·698. It is soluble in hot water; on cooling, crystals of hydrated calcium iodate $(Ca(IO_3)_2+6H_2O)$ separate, leaving the calcium chromate in solution. The simple calcium *iodate* $Ca(IO_3)_2$, called *lautarite*, occurs in the same deposits.

L. J. S.

DIFFRACTAIC ACID, a lichen acid.

DIFFUSION. In any gaseous mixture or liquid solution the composition ultimately becomes the same whatever the original distribution of the gaseous or dissolved substances may have been. In very large systems, as, for example, the atmosphere, there is a small change in composition with height above the earth's surface which is due to the change in gravitational attraction with the size of the molecule. In the laboratory or factory this effect is negligible except when the gravitational or accelerating force becomes very large as in the high-speed or *ultra-centrifuge*. Abnormal separations of the above type will not be considered in the present article. The process by which the condition of equilibrium is reached is termed *diffusion* and it depends not on the circulation of the unequally distributed substance as a whole, but on the vibrations of individual molecules. According to the kinetic theory a mass of gas which macroscopically is at rest, is actually the scene of great activity on the part of the constituent molecules. These move with a high velocity and alter the direction of their motion only after they collide with one another or with the walls of the containing vessel. The occurrence of diffusion in gases thus becomes intelligible, and there is ample experimental evidence for extending the kinetic theory to the liquid state and for considering that the molecules therein are also in a state of constant motion. Even in solids the atoms can, under certain conditions, change their position in the crystal lattice, and a large number of examples of diffusion through solids are now known.

Diffusion of Gases.

The upward diffusion of heavy vapours, *e.g.* bromine, into lighter gases has always been a popular lecture experiment, and in the latter part of the last century much work was done in investigating the quantitative laws that governed this process (*see* Loschmidt, Sitzungsber. Akad. Wiss. Wien, 1870, **61**, 367; 1870, **62**, 468; von Obermeyer, *ibid.* 1880, **81**, 1102; 1882, **85**, 147, 748; 1883, **87**, 188; 1887, **96**, 546; Waitz, Ann. Physik, 1882, **17**, 201, 351; Lonius, *ibid.* 1909, **29**, 664; Brown and Escombe, Phil. Trans. B, 1900, **193**, 223). Many experimental difficulties are met when direct diffusion experiments are attempted, and it is much easier to study diffusion through porous plugs or through small apertures (effusion). In the above cases Graham ("Chemical and Physical Researches," T. and A. Constable, at the Edinburgh University Press, 1876, pp. 44, 88) was able to show that the volumes of different gases diffusing under standard conditions in a given time were inversely proportional to the square roots of their densities. Knudsen (Ann. Physik, 1909, **28**, 75) obtained the same result when gases were allowed to pass through a capillary tube (transpiration). The above relationship holds only approximately unless the mean free path of the gas molecules is large compared with the aperture through which it is being driven—with a large hole the phenomenon is obviously one of the viscous flow and not diffusion. The larger the above ratio becomes the better is Graham's law obeyed (*see* Timoféeff, Z. physikal. Chem. 1890, **6**, 586; Donnan, Phil. Mag. 1900, **49**, 423; Emich, Monatsh. 1903, **24**, 747; Knudsen, Ann. Physik, 1909, **28**, 999). The study of diffusion in gases has been continued by M. Trautz and co-workers as part of a general investigation into gaseous mixtures (*see* Trautz and Müller, Ann. Physik, 1935, [v], **22**, 313). Their work has been criticised by J. Kuusinen (Ann. Physik, 1935, [v], **24**, 445). The problem of calculating diffusion velocities in factory plant has been studed by W. Roth (Arch. Eisenhüttenw. 1934–35, **8**, 401), where equations suitable for the solution of practical problems are given. B. Kries and N. Seljakov (Z. Physik, 1935, **94**, 134) working on mixtures of carbon dioxide and air have studied the conditions of diffusion at high pressures. The evaporation and diffusion of solvent vapours into air has considerable technical importance. E. R. Gilliland (Ind. Eng. Chem. 1934, **26**, 681, 1093) has measured the velocity of these processes for a number of liquids including water, butyl alcohol, and toluene, and, to facilitate reference, the results are represented graphically. The process of evaporation has been shown to consist of diffusion of the vapour from a *supersurface* layer into the gas phase and this diffusion is governed by the ordinary kinetic laws (E. Preston, Trans. Faraday Soc. 1933, **29**, 1188 ; 1935, **31**, 776, 1093). An ingenious apparatus for measuring the diffusion of vapours of volatile solids through gases is described by B. Topley and R. Whytlaw Gray (Phil. Mag. 1927, [vii], **4**, 873). A small sphere of the substance under investigation is suspended from a fine quartz fibre which has been wound into a spiral, thus forming a spring balance[1] which enables the loss in weight of the bead to be measured directly, the vapour being taken up by an adsorbent which is spread on the sides of the container. An accuracy of 2% was obtained for the passage of iodine vapour through air at temperatures between 14° and 30°C.

The principles of the diffusion of gases and vapours have important applications in the designing of *pumps* for high vacuum purposes. They have also been utilised by G. Hertz (Z. Physik, 1934, **91**, 810 ; *see also* Barwich, *ibid.* 1936, **100**, 166) in constructing an apparatus which enables the isotopes of the elements to be separated. One of the units from which the apparatus was built up is shown diagrammatically in the fig. I. The gas enters the unit through a glass tube A in the direction shown by the arrow. It passes into a special porcelain diffusion tube B, which, by means of a grading glass, can be fused to the rest of the apparatus. A light fraction diffuses through B and is collected in the glass jacket C; it is pumped off and circulates with the gas in the previous unit. The remaining gas passes into another porous tube D through which a sample of medium density gas passes ; the light fraction from the next unit is added to this and the mixture recirculated by means of a pump P. Finally the heavy remainder of the gas passes through E to the next unit where the whole cycle of operations is repeated. Thus in each unit there is a continuous process of separating the gas into three fractions, and by increasing the units it is possible to obtain any desired degree of separation. Herz has separated deuterium from hydrogen, also the neon and oxygen isotopes ; indeed, once it is working, even small differences in density lead to effective separations.

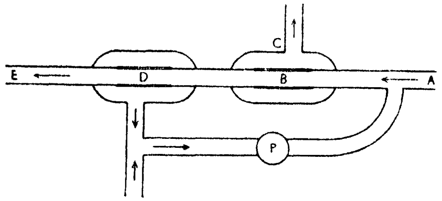


FIG. 1.

DIFFUSION THROUGH METALS.—The passage of a gas across a diaphragm takes place not only when the diaphragm is porous but also if it has the power of dissolving or absorbing the gas. For example, the ease with which hydrogen will pass through hot platinum or palladium sheet has been known for many years. More recently further examples have been investigated and most of them have technical applications either in the wireless valve or metal industries. The more important of these papers are tabulated below.

N_2 through **Cr.**—G. Valensi, J. Chim. phys. 1929, **26**, 152, 202.

H_2 through **Cu.**—E. O. Braaten and G. F. Clark, Proc. Roy. Soc. 1936, **153**, 504 ; A. F. H. Ward, *ibid.* 1931, A, **133**, 506, 522.

O_2 through **Cu.**—F. Wilkins, *ibid.* 1930, A. **128**, 407.

H_2O through **Cu** and N_2 through chrome iron.—J. H. De Boer and J. D. Fast, Rec. trav. chim. 1935, **54**, 970.

He through silica.—E. O. Braaten and G. F. Clark, J. Amer. Chem. Soc. 1935, **57**, 2714 ; Barrer, J.C.S. 1934, 387.

H_2 through **Ni, Cu, Mo** and **Fe** ; N_2 through **Mo.**—C. J. Smithells and C. E. Ransley, Proc. Roy. Soc. 1935, A, **150**, 172.

H_2 through **Al.**—*Idem, ibid.* A, 1935, **152**, 706.

CO through **Ni.**—*Idem, ibid.* A, 1936, **155**, 195 ; A, 1936, **157**, 292.

H_2 through **Pd.**—V. Lombard and C. Eichner, Bull. Soc. chim. 1933, [iv], **53**, 1176, *ibid.* 1935, [v], **2**, 1555; Compt. Rend. 1935, **200**, 1846; *ibid.* 1936, **202**, 1777.

O_2, NH_3, **S** and **P** through **Fe.**—A. Bramley, F. W. Haywood, A. T. Cooper, and J. T. Watts, Trans. Faraday Soc. 1935, **31**, 707.

As a result of the above work the processes involved during the diffusion of gases through metals are known in outline at least. The first fundamental consideration is whether the gas passes through the crystals of the metal or penetrates through minute cracks and the filling at the crystal boundaries. Smithells and Ransley were able to show that the rates for the passage of hydrogen through fine and through large crystalline iron were identical and that diffusion must be through the body of the metal. On the other hand, Wilkins (*l.c.*) and Ward and Wilkins (Z. physikal. Chem. 1929, **144**, 259) showed that in the case of oxygen through copper considerable lateral penetration round the boundaries occurs. A formula for the velocity of diffusion D across a metal plate from a pressure p on one side to zero pressure on the other was suggested by Richardson, Nicol, and Parnell (Phil. Mag. 1904, **8**, 1), who gave

$$D=\frac{k}{d}\sqrt{pT}\cdot e^{-\frac{E}{RT}},$$

where k and E were constants, d was the thickness of the metal, T the absolute temperature, and R the gas constant. This equation ignores the effect of the surface of the metal in adsorbing the gas and it is now considered that unless this occurs the gas cannot penetrate the solid. Thus nitrogen will pass through iron or molybdenum but not through copper or nickel, while the inert gases will pass through glass and silica but not through metals (Barrer, *l.c.*; S. Bern-stein, Compt. rend. Acad. Sci. U.R.S.S. 1934, **1**, 230 ; H. Dünwald and C. Wagner, Z. physikal. Chem. 1934, B, **24**, 53). Smithells and Ransley have shown that the adsorbed film must be allowed for before the Richardson equation would represent their experimental results. They used the following modification for the change of D with p at constant temperature:

---

[1] The quartz spring is usually spoken of as a McBain Microbalance.

$$D=\frac{k}{d}\sqrt{p}\left(\frac{\alpha p}{1+\beta p}\right)$$

The values of the constants α and β agree with those obtained from direct adsorption measurements and the necessity for adsorption to occur before diffusion is possible seems clearly established. It may be noted that the adsorption process would more easily allow the molecules of gas to be split into atoms, and the relationship $D \alpha p^{\frac{1}{2}}$ indicates that diffusion should occur in that state. Ward (*l.c.*) considers the existence of atoms improbable, but B. Duhm (Z. Physik, 1935, **94**, 434) has shown that for the case of hydrogen and palladium true dissociation into atoms can occur.

In a recent communication J. Lynch (Nature, 1937, **40**, 363) has suggested that the mechanical properties of metals may be considerably affected by the solution of gases in them. In support of this contention he reported that the rigidity of a palladium wire was decreased by over 20% when it contained 450 times its volume of dissolved hydrogen.

Diffusion of Liquids and Dissolved Substances.

The foundation of our knowledge of this subject was laid by the classical experiments of Thomas Graham (" Chemical and Physical Researches," T. & A. Constable, 1876, pp. 444–600). In his experiments, 700 c.c. of water were placed in a cylindrical jar and then 100 c.c. of the solution to be diffused were carefully conveyed to the bottom of the jar with the aid of a pipette. After a suitable time portions of 50 c.c. were successively drawn off from the top ; these portions evaporated to dryness, and the amount of substance that diffused into each layer was thus ascertained. Graham's comparative experiments on the diffusive power of different substances in aqueous solution led him to draw a distinction, which has become of the highest importance, between the behaviour of easily crystallisable substances and that of substances which are marked by the absence of the power to crystallise. So far as diffusibility is concerned, the distinction in question is based on the following figures, representing approximate times of equal diffusion : hydrochloric acid 1, sodium chloride 2·3, sucrose 7, magnesium sulphate 7, albumin 49, caramel 98. The difference in diffusive power of crystalloids and colloids is very evident from these figures.

The significance of the quantitative results obtained by Graham was emphasised by Stefan (Sitzungsber. Akad. Wiss. Wien, 1878, **78**, [ii], 957 ; 1879, **79**, [ii], 161), who showed that they were in harmony with Fick's diffusion law, which states that the diffusion of substances in aqueous solution is comparable with the distribution of heat in thermal conductors. Fick's Law is expressed by the formula

$$dS=-D\cdot q\cdot\frac{dc}{dx}\cdot dt,$$

where dS is the amount of substance crossing a section of the diffusion column in time dt, the sectional area of the column being q sq. cm. and dc/dx being the concentration gradient. The constant D is known as the diffusion coefficient. Stefan published tables from which the diffusion coefficient could be obtained directly from the analytical results after the solution had been divided into four portions. The method was modified by Öholm (Z. physikal. Chem. 1904, **50**, 309) and it is sometimes called after him. Its modern form is described by D. Krüger and H. Grunsky (*ibid.* 1930, **150**, 115 ; 1934, **170**, 161). A special apparatus for dividing the liquid into portions after diffusion was devised by E. Cohen and H. R. Bruins (*ibid.* 1923, **103**, 349), who carried out some extremely careful determinations of the diffusion of symmetrical tetrabromoethane into tetrachloroethane between the temperatures of 0·44° and 51·10°C. They discovered deviations from Fick's Law amounting to about three times the magnitude of the possible experimental error. In any method the time required for diffusion to occur is considerable, and there is consequently ample opportunity for the solutions to be mixed by convection currents or by shaking, unless the apparatus is very firmly bedded and the temperature remains absolutely constant. These difficulties have been largely overcome by the introduction of a micro method by R. Fürth (Physikal. Z. 1925, **26**, 719). The cell is approximately 10×15×1 mm. and is mounted on the stage of a microscope through which the progress of diffusion can be observed. Results that are accurate to ±5% can be obtained in experiments lasting only 15 minutes. The method has been carefully worked out by K. Sitte and can be used with very dilute solutions. Full details of the experimental precautions are given in the following series of papers and the complete apparatus is now marketed by Karl Zeiss under the name of " Mikrodiffusionsapparat nach Fürth & Zuber " (R. Fürth, Z. Physik, 1932, **79**, 275 ; R. Zuber, *ibid.* 280, 291 ; R. Zuber and K. Sitte, *ibid.* 306, 320 ; R. Fürth and R. Zuber, *ibid.* 1934, **91**, 609 ; K. Sitte, *ibid.* 617, 622, 642, 651).

A third method of measuring diffusion coefficients which is capable of giving very accurate results is to measure the amount of material that penetrates a fine sintered glass filter. The method was discovered by J. H. Northrop and M. L. Anson (J. Gen. Physiol. 1929, **12**, 543), and the details have been worked out by J. W. McBain and co-workers (J. Amer. Chem. Soc. 1931, **53**, 59 ; 1933, **55**, 432, 545). They have made numerous measurements with the apparatus and have used it in particular for the investigation of large molecules. They have shown that colloidal particles can be made to diffuse normally and that the rate can be used as a method of determining their molecular weight. Thus a value of 34,000 was obtained for egg albumin at its isoelectric point, which is in remarkable agreement with Svedberg's values of 34,500±1,000 by sedimentation equilibrium and 34,000 by osmosis. It is interesting to note that Svedberg could not obtain satisfactory values by diffusion, which McBain attributes to the use of buffer solutions, which he points out are difficult to maintain at identical concentrations on both sides of the diaphragm; secondly, they may cause a change in the size of the molecule under investigation, and thirdly, make analysis more difficult (*see* McBain, C. R. Dawson and H. A. Baker, J. Amer. Chem. Soc. 1934, **56**, 1021). Contributions to the mathematics of the theory of diffusion have come from T. Katsurai and K. Kawashimo (Kolloid Z. 1936, **75**, 37), also from W. G. Eversole and E. W. Doughty (J. Physical Chem. 1935, **39**, 288), but the future development of the subject seems to call for the systematic tabulation of accurate data.

The difference in the rate of diffusion of heavy and light molecules through suitable membranes has been utilised for the removal of electrolytes from colloidal particles by dialysis. The membrane selected, however, is as far as possible semipermeable and consequently the process really belongs to the phenomena of osmosis.

Since the time of Graham the majority of experiments have confirmed that Fick's Law is at least approximately obeyed. A number of examples have, however, been found of materials that diffuse very much faster than anticipated and these substances were said to exhibit *anomalous diffusion*. This was first observed by R. O. Herzog and A. Polotzky with dyestuffs (Z. physikal. Chem. 1914, **87**, 449); other examples, which were found, generally involved natural products, and explanations, like specific reaction with the solvent or lack of purity of the materials, were advanced. These had to be abandoned when H. Freundlich and D. Krüger showed that similar deviations could be obtained with substances of small molecular weight (Trans. Faraday Soc. 1935, **31**, 906). For example, a solution of quinone diffusing into water obeys Fick's Law, but if both solutions are normal with respect to potassium sulphate anomalous results are obtained. The whole subject is critically reviewed by the above authors and they have shown that the anomalous results are attributable to the concentration gradient of the quinone causing the uniformly distributed substance (potassium sulphate) also to diffuse, owing to a mutual change in the solubility of the two solutes. In consequence, in the course of the diffusion process, a thin layer of the liquid on the border line of the two solutions becomes less dense than the solution immediately above. This inadmissible density gradient produces convection currents which obscure the normal process of diffusion. The correctness of this assumption was proved by the fact that the abnormality disappeared when care was taken that the solution above was to a sufficiently marked degree less dense than the one below. It should be noted that the phenomenon occurs only in the boundary layers, and consequently the sharpness of the boundary between the two liquids is not affected.

Diffusion of Solids.

The possibility of diffusion processes occurring with solid materials was indicated by the manufacture of steel by the cementation process; but in spite of its importance industrially, it is only recently that much published work has appeared on the subject. The first example of solid diffusion to be studied was that of gold into lead; this was shown by Roberts-Austin (Phil. Trans. 1896, **187**, 383) to occur to an appreciable extent in 40 days at temperatures between 100° and 200°C. In a subsequent paper (*ibid.* 1900, **67**, 101) it was stated that the process could be detected at room temperatures but that time had to be measured in periods of years. A. E. van Arkel (Metall-Wirt. 1928, **7**, 656) introduced an ingenious method of following diffusion when he coated a copper wire with a layer of nickel by electrolysis and was then able to detect any change by the variation of electrical conductivity of the composite wire. He found that the transfer of metal became appreciable above 800°C. O. Tanaka and Matano (Mem. Coll. Sci. Kyoto, 1931, **14**, A, 59, 123) studied the temperature coefficient for the diffusion of silver into gold and of nickel into copper; and the same measurements were made for gold into lead by G. von Hevesy and W. Seith (Z. Elektrochem. 1931, **37**, 528).

W. Seith and co-workers have in recent years published a series of excellent experimental papers. Using a radioactive indicator—thorium B—they followed its movement into crystals of lead and showed that in this symmetrical lattice the rate was practically the same in any direction (Z. Elektrochem. 1933, **39**, 538). The experiments were then repeated with bismuth and it was found that the diffusion in a direction perpendicular to the crystalline axis was very much faster than when it was parallel to it. A technique was then worked out by which the course of diffusion could be followed by cutting thin layers of the metal and finding their composition by spectrum analysis. The rate of movement of magnesium, cadmium, nickel and mercury in lead; lead, mercury and platinum in cadmium; and platinum into zinc were then determined (*ibid.* 1934, **40**, 318; Z. Metallk. 1932, **24**, 193). The results obtained were then checked by measurements for a series of metals diffusing into silver at temperatures between 650° and 895°C. (Z. Elektrochem. 1936, **42**, 570). The authors have been able to show that in general Fick's Law is obeyed and that diffusion D varies with temperature T according to the formula

$$\log \mathrm{D} = -\mathrm{A}/\mathrm{T} + \mathrm{B},$$

where A and B are constants. Similar conclusions were reached by A. Bramley and co-workers for the diffusion of carbon, sulphur, nitrogen and phosphorus into iron and steel (Trans. Faraday Soc. 1935, **31**, 707). The effect of a second element on the diffusion of a third was also studied with very interesting results. The presence of 0·5% of carbon reduced the velocity of the movement of sulphur by one half. On the other hand, the presence of sulphur or phosphorus almost entirely prevents the movement of carbon and, in the case of phosphorus, the carbon is driven before it into the metal. The penetration of nitrogen is of particular importance owing to its application to the hardening of special steels. It was found that the presence of oxygen favoured the nitriding process, but when the specimen was reduced by hydrogen for 200 hours before nitriding, instead of a minimum value being obtained, the process was nearly as fast as in the presence of the optimum amount of oxygen. Anomalies of this type require much experimental work for their elucidation, but, since traces at least of these elements may be expected in any commercial sample of steel, they may prove to be of the utmost importance.

R. H. P.

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